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EXPLORATION OF VANADIUM-BASE ALLOYS

ALBERT S. YAMAMOTO

WILLIAM ROSTOKER

ARMOUR RESEARCH FOUNDATION

JANUARY 1955

WRIGHT AIR DEVELOPMENT CENTER

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UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report was prepared by the Armour Research Foundation of Illinois Institute of Technology, Chicago, Illinois, under USAF Contract No. AF 33 (038)-8517. The contract was initiated under Task No. 73510, "Rare and Unusual Metals" (formerly RDO No. 615-16, "Rare and Unusual Metals"), and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Lt C. M. Wayman acting as project engineer.

ABSTRACT

This is the third annual report summarizing the results of work performed during the period May 15, 1953 to June 14, 1954. The oxidation study on vanadium alloys has been further pursued and the conclusion has been reached that satisfactory oxidation resistance at elevated temperature of vanadium-base alloys cannot be rendered by alloying alone but possibly by electroplating. Major efforts have been directed toward evaluating the elevated temperature tensile and stress-rupture strengths of the alloys under development. Carbon additions have proven beneficial as far as the forgeability is concerned. In certain cases, however, superior tensile ductilities are observed while no effect in stress-rupture behavior results. The current availability of less expensive vanadium-aluminum alloy produced by the alumino-thermic reduction process has promoted a feasibility study of its use. It is found that the alloys made of this are as competitive in mechanical properties as the equivalent alloys based on the very expensive calcium-reduced vanadium metal.

A range of alloy compositions containing additions of titanium and aluminum have shown stress-rupture behavior which is as good or marginally better than the best titanium-base alloys.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:
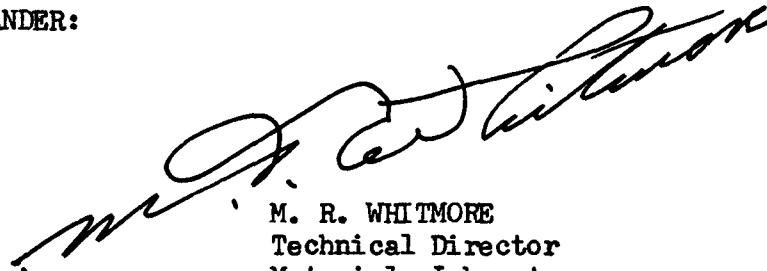
M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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EXPLORATION OF VANADIUM-BASE ALLOYS

I. INTRODUCTION

This report includes the results of research performed over the past year directed towards the development of potentially useful vanadium-base alloys. It may also be regarded as a generalized summary of the results of the last three years' work.

In the first year of work, studies on alloying behavior, resultant hardening phenomenon and characteristic oxidation of vanadium were made (WADC Tech. Report 52-145, Pt 1). On the basis of this preliminary work, the second year's program was initiated towards the evaluation of forge-ability and mechanical properties of vanadium and its alloys at room temperature and at elevated temperatures. At the same time more extensive studies on the improvement of oxidation resistance of vanadium by alloying were conducted. A cursory investigation on vanadium-oxygen binary phase relationship was made (WADC Tech. Report 52-145, Pt 2).

The work in the third year was confined to the continued studies on oxidation resistance, tensile and stress-rupture properties of selected vanadium alloys. It was demonstrated that satisfactory oxidation resistance of vanadium or vanadium alloys cannot be achieved by simple alloying techniques. To circumvent this problem electroplating of selected alloys with nickel was attempted and promising results were obtained.

Carbon additions into vanadium alloys have been found beneficial in improving forgeability. In some cases it imparted superior ductilities to alloys while there was little effect on stress-rupture strengths.

The stress-rupture behavior of a wide range of alloys was explored. Despite the limited survey, certain vanadium alloys demonstrated their promising quality when judged in terms of a stress-to-rupture versus density.

The currently available vanadium source by the alumino-thermic reduction process could be a solution in future application from the view-point not only of its economy but also of its good high temperature properties when alloyed properly.

II. EXPERIMENTAL METHODS

A. Melting

All alloys were produced by melting of the elemental components in their proper proportions in a non-consumable electrode, water-cooled copper

crucible, arc-melting furnace. Ingots were generally of the sizes 125 or 200 grams. Compositions referred to in the test of this report unless otherwise specified are nominal. Chemical analyses of carbon added to vanadium alloys were conducted as well as of the melted vanadium-carbon (approximately 20%) master alloy.

The vanadium metal used as an alloying base was obtained from the Electro Metallurgical Division of the Union Carbide and Carbon Corporation in the form of selectively sized chips. The metal was melted in the as-received form. The total interstitial content (carbon, oxygen and nitrogen) was reported 0.22%.

Titanium was supplied by Titanium Metal Corporation in the form of sponge. Electrolytic chromium was obtained from the Electro Metallurgical Corporation and pure aluminum from the Aluminum Company of America. These were all of commercially pure quality. As a carbon addition source, spectrographic graphite rods were acquired from the National Carbon Company.

B.   Forging

Ingots were forged to 1/2 in. diameter rods for tensile and stress-rupture test specimens. All forging was performed on a drop hammer equipped with open dies. Forging temperatures varied from 1150° to 1350°C depending on the stiffness of the alloy. Preheating was conducted in gas-fired muffle furnaces with no protective atmosphere. From the experiences in the past two years, contamination of ingots could be minimized by limiting the total time in the furnace to less than 15 minutes.

C.   Tensile Testing

Tensile test pieces were machined from 1/2 in. diameter forged rods into standard tensile specimen of the following specifications: test diameter - 0.252 ± 0.001 in., gage length - 1 in., overall length- 3 in. Testing was performed in a conventional Baldwin-Southwark, hydraulically-operated, universal testing machine. When the alloy was known to be ductile from prior knowledge, yield point was measured with an optical extensometer.

For tensile testing at elevated temperatures between 100° and 900°C, controlled heating and an adequate uniform temperature zone were provided by a vertical tube furnace surrounding the sample during the test. The temperature was controlled by a commercial controller to within ± 5°C. A uniform temperature zone of about 2 in. was maintained. Actual testing temperatures were measured by two thermocouples bound to the test length of the specimen.

No protective measure against oxidation at elevated temperatures was provided since the testing time was very short.

D.   Stress-Rupture Testing

Lever-arm type stress-rupture test units were used in this work. Test pieces employed were of the standard 0.252 in. diameter tensile test type

specimens. Extensometers were attached to the shoulder of the test specimens to obtain stress-rupture data. Testing was earlier conducted at three temperatures = 500°, 600° and 700°C. In the later stage of the work, however, it was confined to two temperature levels, at 500° and 600°C. It has been the practice that three recording thermocouples were attached to the test section of each specimen. The temperature control over the gage length by using Marshall tube furnaces and Wheelco controllers was maintained within ± 1°C.

E.   Oxidation Testing

Rates of oxidation of vanadium alloys at temperatures above 675°C (i.e. melting point of V_2O_5) were measured. Cylindrical specimens (0.95 cm diameter by 0.95 cm long) were suspended in a vertical tube furnace in a slow stream (5 liters per minute) of filtered and dry air. At the conclusion of the tests the samples were mounted in bakelite and were cross-sectioned. The residual cross section of metal was then measured under a microscope. The results obtained by this technique can be correlated to any other oxidation experiment irrespective of weight gain or weight loss. In fact, the residual metal cross section, rather than weight change, renders the more direct and vital information.

The same conditions and equipment were used for study of the effectiveness of nickel plating on a V-40% Ti-5% Al alloy. In this case, endurance of nickel plates of various thickness at two different temperatures (700° and 800°C) after a 96 hour exposure was observed. A minimum effective thickness of nickel coating required for 96 hours' endurance at 800°C was so obtained.

Plating procedure is described in detail in an appendix attached at the end of this report.

III.   OXIDATION RESISTANCE OF VANADIUM ALLOYS

Vanadium can form about five different oxides of which the most oxygen-rich, V_2O_5, has a uniquely low melting point of about 675°C. It was demonstrated early in this program of research that molten V_2O_5 will drip off from a specimen of vanadium suspended in air at 700°C. By continuous exposure of the sub-oxides to fresh oxygen supply, the oxidation rate follows a linear relationship. The slope of the oxidation rate curve is sufficiently steep that a cylindrical sample about 1 cm diameter will be completely converted to oxide in 35-40 hours of exposure to freely circulating air. Below 675°C, the oxides are solid and tightly adherent. Oxide penetration at 600°C for one month was less than 0.4 mm in all instances and, in most instances, less than 0.1 mm. From these general observations it is apparent that oxidation is not a serious problem below 675°C. However, above that temperature, the problem is of such a serious nature as to preclude the usefulness of vanadium unless something can be done to modify the catastrophic oxidation.

Over the past two years a considerable proportion of the total research effort has been devoted to improving the oxidation characteristics of vanadium alloys. This phase of work has followed four successive steps:

i) Comprehensive study of the oxide melting characteristics of 13 alloying elements in binary alloys covering very wide ranges of composition. This was followed by more restricted studies on ternary alloys of the type V-Ti-Cr and V-Ti-Al.

ii) Measurement of the rate of oxide penetration at 700°C for up to 5 hours on 28 binary and 19 ternary selected alloys.

iii) Measurement of the oxidation penetration at 700°, 800°, 900°C after 96 hours' exposure on selections from 18 binary and ternary alloys.

iv) Development of surface protection by diffusion alloying and electroplating.

The study of oxide melting characteristics showed that, within forgeability ranges, no alloy additions would significantly raise the melting point of the surface oxide. It was, however, noted that certain alloy additions notably Ti, Cr, Al and Si in amounts which still permitted forgeability, had the effect of rendering the molten oxide more viscous and hence more reluctant to drip off. The possibility therefore existed that a liquid envelope of molten oxide could exert a protective action against further oxidation.

Measurement of the rate of oxide penetration over a 5 hour period at 700°C confirmed that a number of alloy additions changed the oxidation reaction curve from linear to parabolic. Because of the wide range of forgeable compositions, it was evident that a large proportion of titanium was a necessary prerequisite to significant oxidation suppression. The program accordingly was directed to 96 hour oxidation rate studies on V-Ti, V-Ti-Cr, V-Ti-Al and V-Ti-Si alloys. On the basis of these tests, a limited number of alloys were further tested for 96 hours at 800° and 900°C.

The results of these tests may be summarized briefly in terms of the alloy compositions at each of three temperatures which are capable of withstanding oxide penetration of less than one millimeter in a 96 hour period:

at 700°C	V + 50% Ti
	V + 40% Ti + 5-10% Cr
	V + 50% Ti + 5-15% Cr
	V + 50% Ti + 5-10% Al
at 800°C	V + 40% Ti + 10% Cr
	V + 50% Ti + 10-15% Cr
at 900°C	none

Unfortunately alloys of the type V + 50% Ti + 5%-15% Cr tested for stress-rupture characteristics at 700°C showed oxidation appreciably in excess of that anticipated from non-stressed specimens. It must be concluded that whatever improvement has been possible by alloying, it is insufficient to prevent serious deterioration of alloy specimens loaded mechanically as might be expected in service.

This conclusion was reached during the past year of research. Accordingly efforts were diverted to developing surface protection for vanadium alloys. This is a less desirable alternative since an oxidation resistant surface layer cannot be expected to be self healing should flaws in the surface coating occur.

Attempts were made to develop protective surfaces by diffusion alloying by packing vanadium alloy specimens in specific metal powders. Pack cementation by Mn, Ni, Co, Si, Cr and Fe was attempted. Diffusion heat treatments used were of the order of 1000°-1200°C for 24 hours. There was a general inability of this method to produce uniform infusion from the metal powders. As a consequence, subsequent oxidation tests showed significant protection at certain points and none at others. It was concluded finally that such methods of producing protective surfaces were not practical even on a laboratory basis.

Considerable effort was devoted to electroplating metals on to vanadium alloy specimens. There are a number of advantages to provide the required surface protection of electroplating.

i) Electrocleaning and plating can be accomplished without too much risk of oxidation. Hydrogen embrittlement can be expected but this can be eliminated by low temperature annealing.

ii) A successful plating procedure can provide a smooth metallic layer which is uniform both in thickness and adherence.

iii) The times for plating are shorter and the equipment simpler than for cementation protection processes.

Manganese, chromium and nickel were chosen as elements to be plated on vanadium. There has been considerable effort directed toward electroplating molybdenum and titanium with nickel and/or other elements and some published information is available.

Korbelak[*] reported that a molybdenum specimen with 3 mils of electro-deposited nickel over a chromium flash withstood oxidation as long as 300 hours at 1800°F (982°C). On the other hand, a nickel plated specimen without the chromium base held up only 24 hours at this temperature.

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[*] A. Korbelak, Plating, 40(10), pp. 1126-1131, Oct. 1953.

Other information by Sutcliffe[*] showed that the oxidation rate of nickel plated titanium was similar to that of nickel on a test of 5 days at 800°C. When the surface film of nickel cracked, the oxidation rate increased to that of the unplated titanium.

Plating experiments were performed on a vanadium alloy containing 40% Ti and 5% Al. This alloy has good tensile properties and stress-rupture strength but is deficient in oxidation resistance.

A 5-mil deposit of manganese was successfully applied to the vanadium alloy although the adherence of the deposit was not very satisfactory. The details of plating procedure are contained in an appendix to this report. The manganese was infused into the vanadium specimens by an anneal at 1100°C for 24 hours in an evacuated Vycor bulb. The specimens so produced were exposed to air at 700°C. Evidence of serious oxidation became apparent after 20 hours. After 96 hours the specimen had almost completely oxidized. It was concluded from these experiments that manganese was not a suitable protective agent.

Plating of chromium on the vanadium alloy was not successful. An adherent deposit of chromium could not be obtained.

Nickel plating proved to be eminently successful. Bright, smooth, and adherent deposits were obtained. The details of the plating procedure are given in an appendix to this report. Cylindrical specimens plated with various thicknesses of nickel were submitted to oxidizing conditions (freely circulating air) at 800°C for 96 hour exposures. One specimen was given a diffusion anneal in vacuum before the oxidation test. A photomicrograph of the diffusion zone is shown in Figure 1. The diffusion bond was obviously good. It appeared from the results that for a flaw -free plate, the diffusion anneal was unnecessary. The results are summarized in Table I. It will be noted that even very thin deposits of nickel were capable of completely preventing oxidation in vanadium.

In order to see the manner of breakdown of the protective action of nickel in event of a surface imperfection, a sawcut was deliberately made to penetrate the nickel plate on a vanadium alloy specimen. The specimen was exposed to air at 800°C for 72.5 hours. Figure 2 shows a cross section of this specimen after exposure. It can be seen that oxidation is mainly confined to the volume of vanadium immediately adjacent to the sawcut but that oxidation gradually penetrates along the vanadium-nickel interface. Under such circumstances, the diffusion anneal treatment following the electroplating operation would probably create a structure capable of inhibiting the action.

In summary it can be stated that no alloy could be developed which would satisfactorily withstand oxidizing conditions above 675°C. However, a protective surface of nickel can be applied to vanadium and its alloys by electroplating which can withstand oxidation for at least 96 hours at 800°C. Essentially a defect-free nickel surface on vanadium of more than 5 mil thickness imparts to the specimen the oxidation resistance of nickel.

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[*] D. A. Sutcliffe, Royal Aircraft Establishment (Great Britain), PB 108808, 4 pp., Dec. 1950.
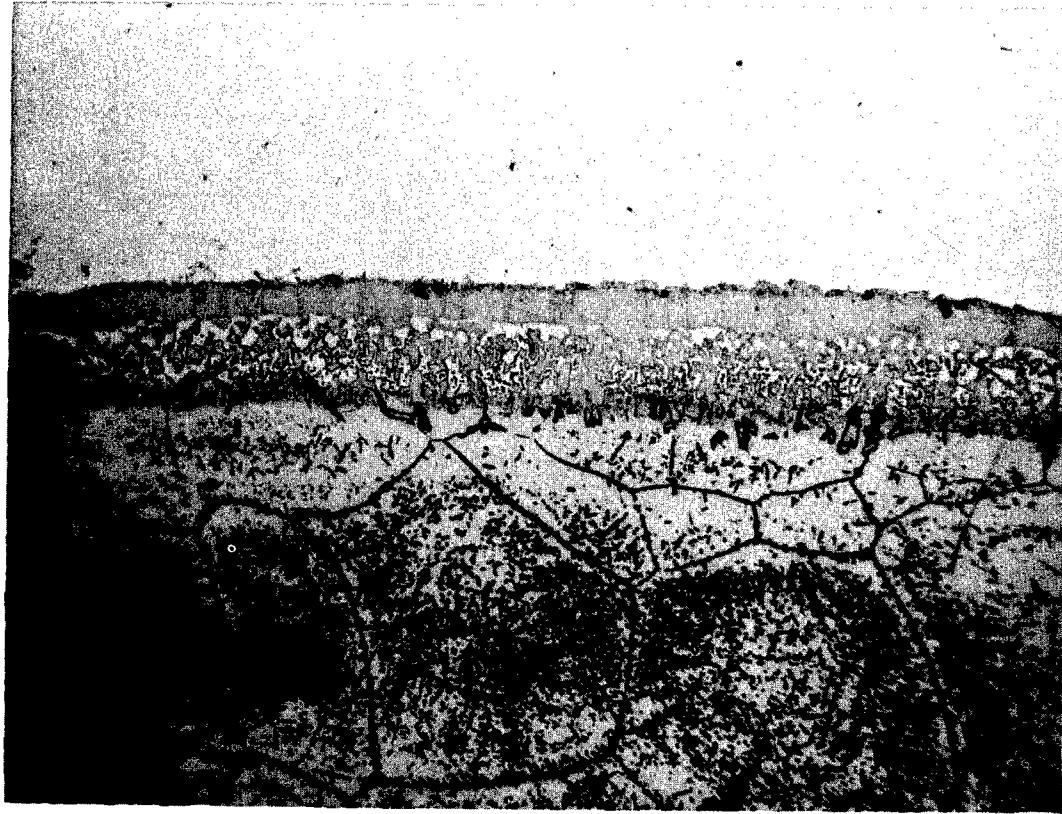
Neg. No. 9175   X 250

Fig. 1

DIFFUSION ZONE BETWEEN V-40% Ti-5% Al ALLOY AND NICKEL
PLATING PRODUCED BY ANNEALING IN VACUM AT 1000° C FOR 24
HOURS.

TABLE I

SUMMARY OF EXPERIMENTS ON THE OXIDATION RESISTANCE

OF A NICKEL PLATED VANADIUM ALLOY (40% Ti-5% Al)

Nickel Plate Thickness	Heat Treatment	Oxidation Test	Notation
23 mils	1000°C-24 hrs.	700°C-96 hrs.	No oxidation
39 mils	1000°C-24 hrs.	800°C-96 hrs.	No oxidation
18-23 mils	none	800°C-96 hrs.	No oxidation
13-17 mils	none	800°C-96 hrs.	No oxidation. Plate flaked off during cutting for examination.
3-5 mils	none	800°C-96 hrs.	Some oxidation attack under the 3 mil plate.
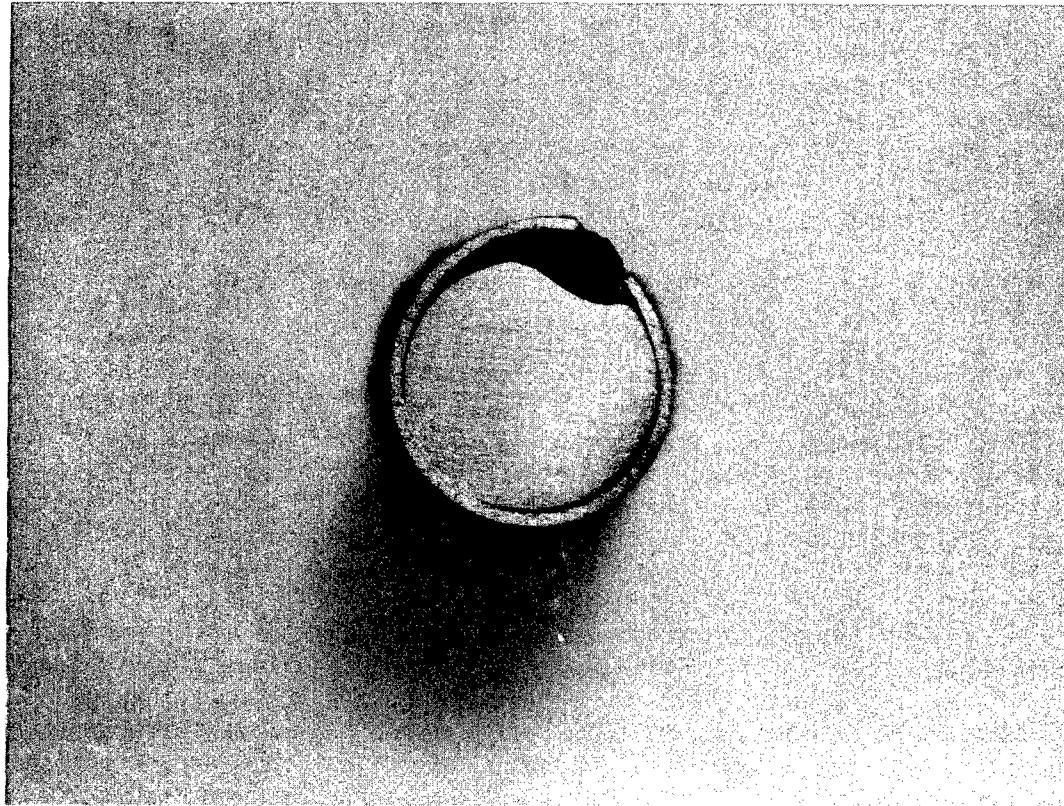
Neg. No. 9245   X 3

Fig. 2

CROSS SECTION VIEW OF OXIDATION DAMAGE TO
SPECIMEN OF V-40% Ti-5% Al ALLOY ELECTRO-
PLATED WITH 20 MILS OF NICKEL(NO DIFFUSION
ANNEAL). THE PLATE HAD BEEN DELIBERATELY CUT
THROUGH BY A SAW PRIOR TO EXPOSURE TO AIR AT
800^0 FOR 72.5 HOURS.

IV. FORGEABILITY OF VANADIUM ALLOYS

All of the work on mechanical properties of vanadium alloys was performed on 1/2 in. diameter rods forged from 125-200 gram arc melted ingots. These ingots were pancake-shaped having approximate dimensions of 1/2 in. thickness by 2-2 1/2 in. diameter. Forging failures generally occurred in the early stages of breakdown of the cast structure. At some alloy compositions more than half of the ingots produced broke under the forge hammer.

In an attempt to improve the creep resistance of certain vanadium alloys by the addition of a dispersed phase, carbon was added to the melts. The carbon appears largely as carbides (V_2C or VC), the solid solubility being very small. It was immediately noted that the melts deliberately innoculated with carbon had superior forgeability. During the past year, carbon additions have been added to a large number of alloys which have marginal forgeability. In almost every instance the forgeability was improved.

The reason for the improvement in forgeability is as follows: The severely chilled solidification conditions existing during the melting operation develop a completely columnar as-cast grain structure in the ingots. Such an as-cast structure is well known to be very disadvantageous for forging. By the addition of carbon, the primary crystallization phase is the carbide (V_2C or VC) which acts either to nucleate vanadium solid solution grains more uniformly throughout the melt or to inhibit oriented growth from the mold walls or both. Macrographs of four alloy ingots with successively higher carbon contents are illustrated in Figure 3. The effective suppression of the columnar grain structure is clearly shown.

Carbon can be added either in the elemental or master alloy form. Analyzed contents agreed more closely with nominal when master alloy additions were used.

V. TENSILE PROPERTIES OF VANADIUM AND ITS ALLOYS

The pattern of evaluation of the mechanical properties of vanadium and its alloys has included in succession room temperature tensile behavior; elevated temperature tensile behavior; and stress-rupture behavior. A wide survey of hardness was included in the first summary report (WADC TR 52-145, Pt 1). Most of the room temperature and elevated temperature tensile testing results were summarized in the second summary report (WADC TR 52-145, Pt 2).

Unalloyed vanadium, in the purity offered by the calcium reduction process, has a very low room temperature yield point (46,600 psi at 0.2% offset) and a low ultimate tensile strength (49,000 psi). Although tensile ductility parameters are poor (24% R.A., 6% Elong.) the annealed metal can be cold rolled to at least 90% reduction in area without intervening anneal.
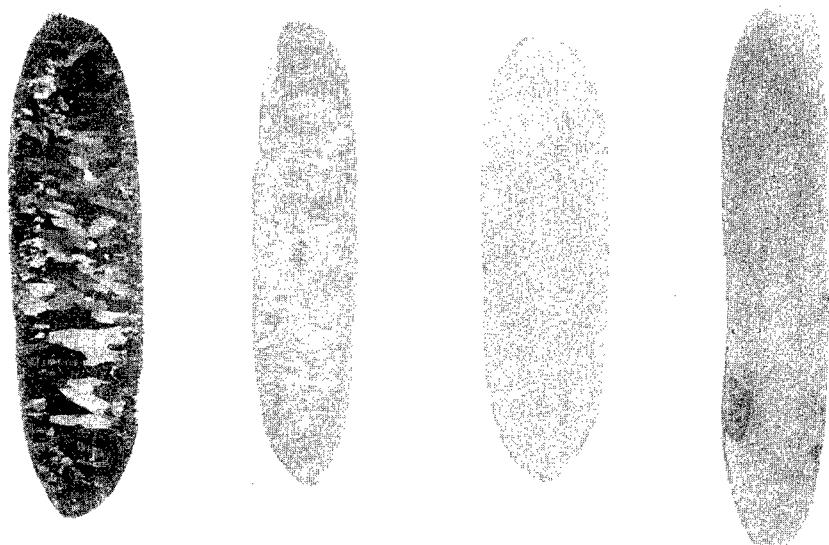
0% C   0.47% C   0.96% C   1.40% C

Neg. No. 7179   X 1

Fig. 3

INFLUENCE OF CARBON ADDITIONS ON THE SUPPRESSION OF COLUMNAR ASCAST GRAIN STRUCTURE IN AN ALLOY V-50% Ti-7% Al.

Except for Ti and Zr, all binary additions to vanadium developed extreme brittleness in the alloys. The V-Ti series was shown to be forgeable and to yield good tensile ductilities up to and beyond 50% titanium. The V-Zr series was limited by hot shortness in forging to less than 3% zirconium. It was therefore obvious that the potentially useful vanadium-base alloys would be polycomponent V-Ti-X in the range 5-50% titanium where X was one or more of other elements added to confer improvement in specific properties. Limitations of funds prevented a very wide survey of the influence of various ternary elements. Effort was concentrated on the additions and the composition ranges which promised both superior oxidation resistance and strength. The results of oxidation rate studies pointed to compositions containing 40-50% titanium and 1-10% of aluminum, chromium or silicon. The principal part of this report concerns itself with the mechanical properties of such alloys.

As discussed in the section on forgeability, it was found of considerable use to add carbon to alloys whose forgeability was marginal. The carbon is almost completely combined as carbides dispersed throughout the body centered cubic matrix. Apart from forgeability effects, the carbides were found to exercise some influence on mechanical properties.

During the past year, the Electro-Metallurgical Corporation of Niagara Falls, New York made available in experimental quantities a new vanadium produced by a process of alumino-thermic reduction of V_2O_5. The product is somewhat higher in interstitial content and has an aluminum content of the order of 13%. It cannot therefore be classed as a "ductile" vanadium. Its main usefulness is as an alloy addition. A typical lot analysis is as follows:

$$V = 84.17\%$$
$$Al = 13.99\%$$
$$Fe = 0.50\%$$
$$Si = 0.40\%$$
$$O = 0.26\%$$
$$N = 0.03\%$$
$$C = 0.03\%$$
$$H = 0.005\%$$

The most significant feature of this material is the price of $10[*] per pound, with reasonable expectation of a lower price, on a larger scale of production. This is to be compared with the current price of $45 per pound for calcium-reduced metal. From this viewpoint, V-Ti-Al alloys which have attractive mechanical properties are potentially competitive even on a price basis with titanium-base alloys for elevated temperature use.

A.   Tensile Properties of Cold Rolled Vanadium Sheet

A two-pound ingot of calcium reduced unalloyed vanadium was forged to block form. After suitable scalping, the forged block was rolled according to pre-calculated schedule so that sheet was produced with various degrees of prior cold reduction and all to the same final gauge (0.056 in.).

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[*] As of June 1954, this price has been reduced to $5 per pound.

Machined test pieces 5 in. long by 1/2 in. wide (test width) were prepared. The test results are summarized in Table II and graphically demonstrated in Figure 4.

The tensile strength of unalloyed vanadium is not markedly increased by progressive cold working. A high ratio of yield to ultimate strength obtains throughout the whole history of deformation. This is also reflected in consistently low percentage elongation values. This behavior is rather unusual for a relatively pure metal. It does not offer potentially good deep drawing qualities. In this respect, alloys containing 5% titanium or 1-2.5% zirconium as reported in WADC-TR-53-178 would be considerably superior.

B.   Tensile Properties of Vanadium Alloys

During the past year, work continued on the evaluation of the influence of various alloying elements on the tensile behavior of vanadium alloys, both at room and at elevated temperatures. The program of study has concentrated on vanadium-titanium alloys with additions of Al, Cr or Si in amounts up to practical forgeability limits. Carbon additions in amounts up to 1.5% (nominal) were made to specific ternary alloy compositions. A number of V-Ti-Al alloys were made from alumino-thermic vanadium. Their behavior was analyzed with and without the presence of carbon additions.

1.   Room and Elevated Temperature Tensile Properties of V-Ti-Si Alloys

A portion of this work was reported in the last summary report. Further results have been obtained and a complete summary of the tensile properties at room temperature of this group of alloys is included in Table III.

Silicon appears to exert a stronger solid solution hardening influence than either aluminum or chromium. A direct comparison might be made between the tensile strengths of vanadium alloys containing 50% titanium and 5% of aluminum, chromium and silicon respectively:

> aluminum: 126,000 psi
> chromium: 133,400 psi
> silicon: 160,200 psi

A rapid evaluation of the influence of silicon on high temperature strengths was made by tensile testing at 900°C a group of alloys containing 50% titanium and progressively increasing amounts of silicon. These results are summarized in Table IV. It is evident that these alloys are all very ductile at 900°C but the tensile strengths are substantially unaffected by silicon content. The comparable binary alloy containing only 50% titanium showed a tensile strength of 20,000 psi at this temperature.

TABLE II

TENSILE PROPERTIES OF COLD ROLLED VANADIUM SHEET

Cold Work %	Yield Strength psi	Ultimate Tensile Strength psi	Elongation %
21	- 61,353	64,493 61,836	3.7 6.3
49	72,222	72,464	6.3
66	77,536 70,773	77,778 71,739	3.7 6.3
80	- 74,879	77,451 75,845	6.3 9.4
86.5	- -	79,263 72,685	3.2 3.7
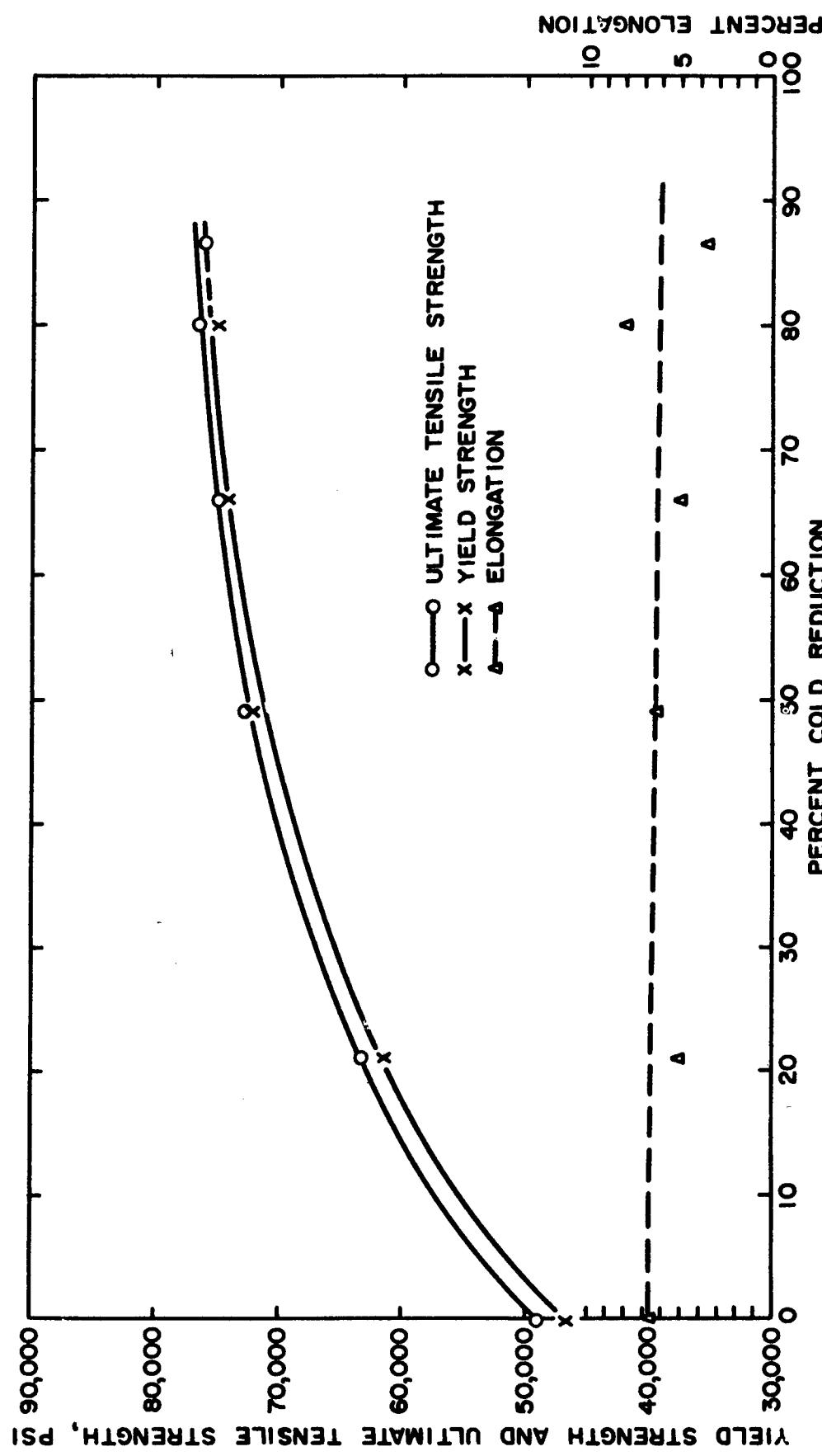
FIG. 4 – TENSILE PROPERTIES OF COLD ROLLED VANADIUM SHEET.

TABLE III

TENSILE PROPERTIES OF VANADIUM-TITANIUM-SILICON ALLOYS

Composition	Ultimate Tensile Strength psi	Elongation %	R.A. %
5% Ti, 0.25% Si	71,500	15.6	37.0
5% Ti, 0.50% Si	68,100	18.8	33.0
5% Ti, 0.75% Si	79,200	21.9	34.0
5% Ti, 1 % Si	82,000	24.0	48.0
5% Ti, 2 % Si	93,000	3.1	10.0
5% Ti, 3 % Si	90,200	3.1	3.0
10% Ti, 1% Si	93,000	29.7	37.7
20% Ti, 1% Si	118,000	21.9	20.2
20% Ti, 5% Si	141,000	0	0
30% Ti, 1% Si	126,400	12.5	10.8
40% Ti, 1% Si	131,000	18.8	25.0
50% Ti, 1% Si	132,000	14.0	15.4
50% Ti, 2% Si	150,000	12.5	17.5
50% Ti, 4% Si	171,200	1.6	0
50% Ti, 5% Si	160,200	4.7	2.8
50% Ti, 6% Si	130,400	0	0
50% Ti, 7% Si	173,200	1.6	0

TABLE IV

TENSILE PROPERTIES OF V-50% Ti-Si ALLOYS AT 900°C

% Si	Ultimate Tensile Strength psi	Elongation %	R.A. %
3	24,000	150	>95
4	20,000	156	>95
5	30,000	103.1	>95
6	20,000	148	>95
7	29,000	126	>95

2. Elevated Temperature Tensile Properties of V-Ti-Al Alloys

A detailed study of the tensile behavior of four alloys in this series was made. These alloys contained:

V + 50% Ti + 5% Al
V + 50% Ti + 10% Al
V + 40% Ti + 5% Al
V + 40% Ti + 10% Al
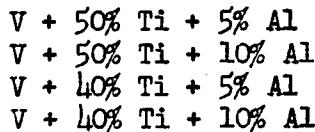
The 10% aluminum level represents the practical limit of forgeability. Summaries of the tensile data are shown in Tables V, VI, VII and VIII. Graphical representations are given in Figures 5, 6, 7 and 8. For comparison the graphs show dotted curves of the tensile behavior of the binary alloy having the same titanium content.

It is quite clearly shown that the ternary additions of aluminum enhance the tensile strengths of V-Ti alloys in some instances without concurrent deterioration of ductility. There seems to be little advantage gained in strength by increasing aluminum contents from 5 to 10%. Ductility losses outweigh strength gains. The differences in strength between the binary alloys and the ternary alloys with the same titanium content tend to disappear at 900°C.

3. Tensile Behavior of Vanadium Alloys with Carbon Additions

Carbon was added as an alloying agent originally as elemental graphite of spectrographic grade. Subsequently it was discovered that not all of intended carbon was generally dissolved into the melt. Deviations from nominal analysis were particularly serious at 1% or more intended carbon levels. Accordingly trends based on nominal analyses must be regarded as very tentative. When it was discovered that the carbon losses as undissolved inclusions were serious, master alloys were developed. These master alloys contained about 20% carbon, (see section on alumino-thermic vanadium based alloys).

The following alloys were tested with various carbon additions:

V + 50% Ti + 5% Cr
V + 50% Ti + 10% Cr
V + 50% Ti + 15% Cr
V + 40% Ti + 5% Cr
V + 40% Ti + 5% Al
V + 50% Ti + 10% Al
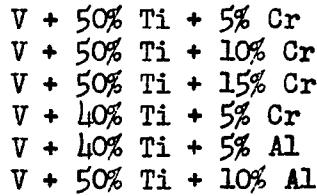
The results are summarized in Tables IX to XIV. Wherever possible comparable data on alloys without carbon additions have been included. Data on the 50% Ti-5% Cr and 40% Ti-5% Al alloys with nominal 0.5% carbon additions were complete enough to represent graphically in Figures 9 and 10.

The results indicate the following conclusions:

TABLE V

ELEVATED TEMPERATURE TENSILE PROPERTIES OF A V-50% Ti-5% Al ALLOY

Temperature °C	Ultimate Tensile Strength psi	Elongation %	R. A. %
RT	126,000	17.2	25.2
100	113,200	20.3	32.6
300	117,400	26.5	35.1
500	110,400	15.6	32.6
600	109,000	13.5	34.3
700	84,600	12.5	15.3
900	19,200	96.8	>95

TABLE VI

ELEVATED TEMPERATURE TENSILE PROPERTIES OF A V-50% Ti-10% Al ALLOY

Temperature °C	Ultimate Tensile Strength psi	Elongation %	R.A. %
RT	84,000	0	0
100	128,400	6.3	18.1
300	117,000	17.0	50.8
500	109,600	6.2	0
	105,600	1.0	1.4
700	104,000	26.2	46.1
900	20,200	103.1	>95

TABLE VII

ELEVATED TEMPERATURE TENSILE PROPERTIES OF A V-40% Ti-5% Al ALLOY

Temperature °C	Ultimate Tensile Strength psi	Elongation %	R.A. %
RT	134,600	23.4	25.8
100	122,200	17.2	29.3
300	115,600	15.6	30.5
500	109,600	9.4	19.5
700	96,600	9.4	16.7
900	35,200	28.2	25.2

TABLE VIII

ELEVATED TEMPERATURE TENSILE PROPERTIES OF A V-40% Ti-10% Al ALLOY

Temperature °C	Ultimate Tensile Strength psi	Elongation %	R.A. %
RT	47,200	0	0
100	72,200	0	0
300	95,600	0	0
500	93,600	0	0
700	92,200	0	0
900	26,000	82.8	79.5
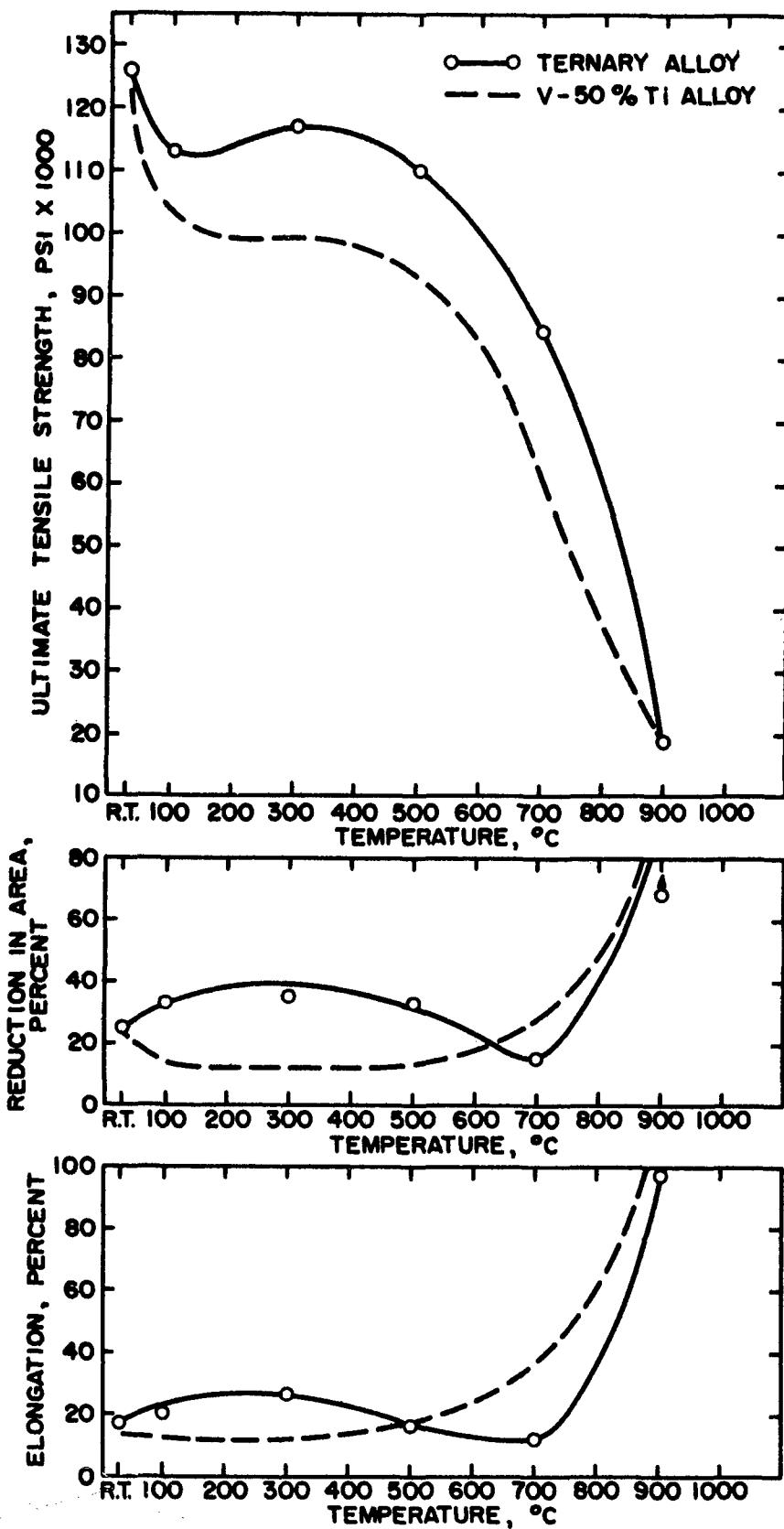
FIG. 5 - ELEVATED TEMPERATURE TENSILE PROPERTIES
OF A V-50% Ti — 5% Al ALLOY.
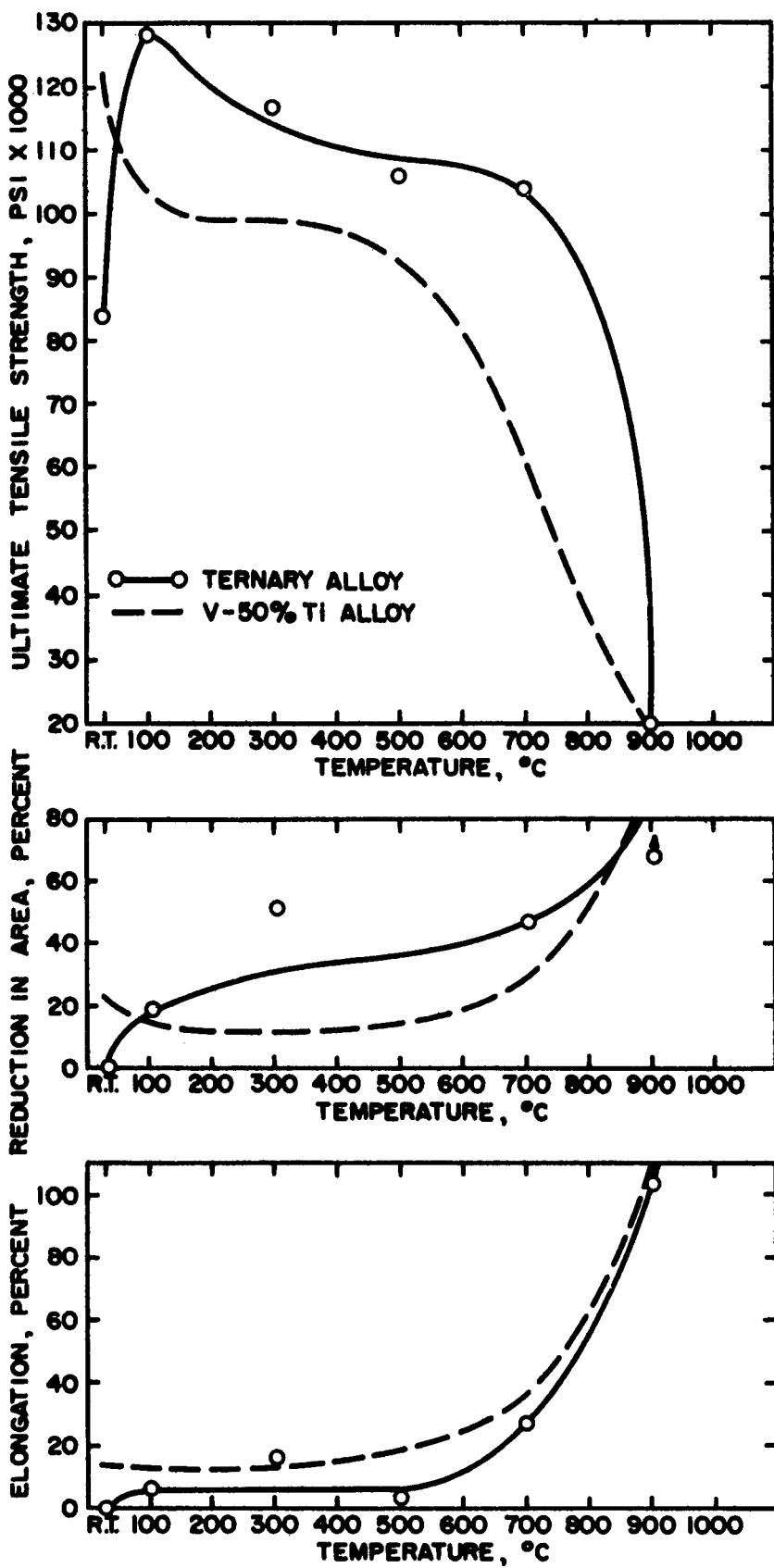
FIG. 6 - ELEVATED TEMPERATURE TENSILE PROPERTIES
OF A V-50%Ti -10% Al ALLOY.
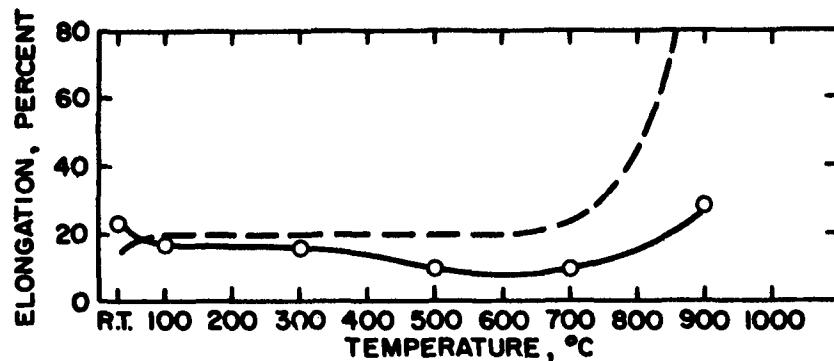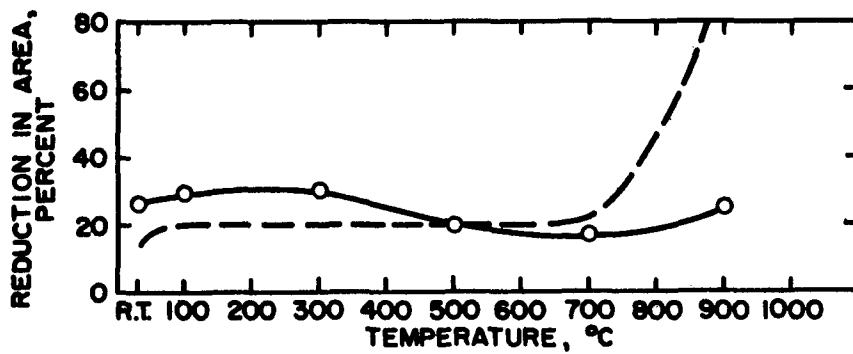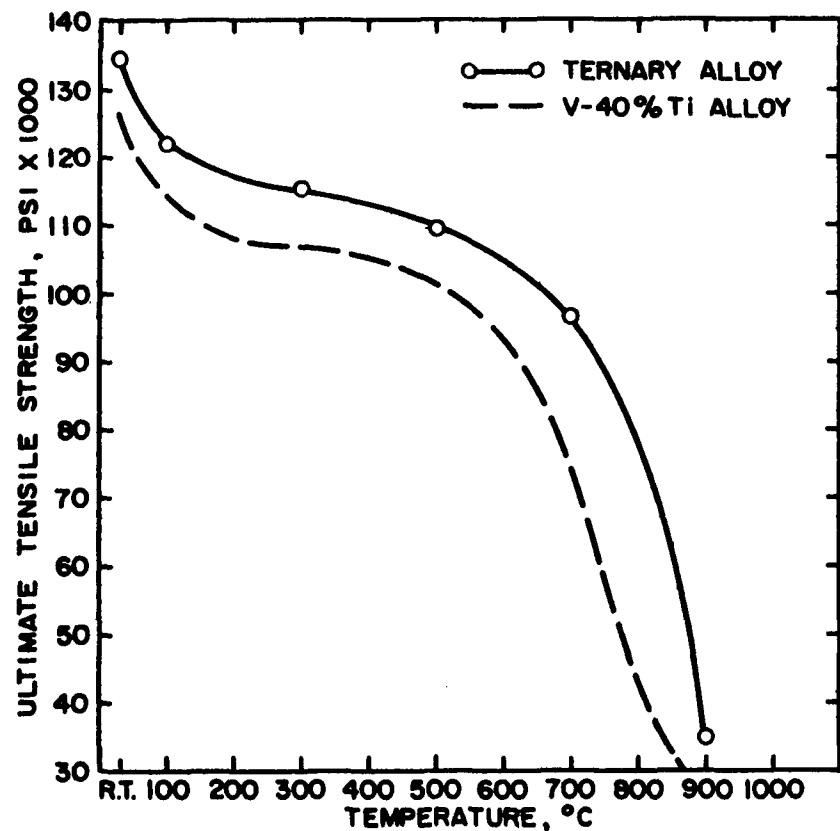
FIG. 7 - ELEVATED TEMPERATURE TENSILE PROPERTIES
OF A V-40% TI - 5% AI ALLOY.
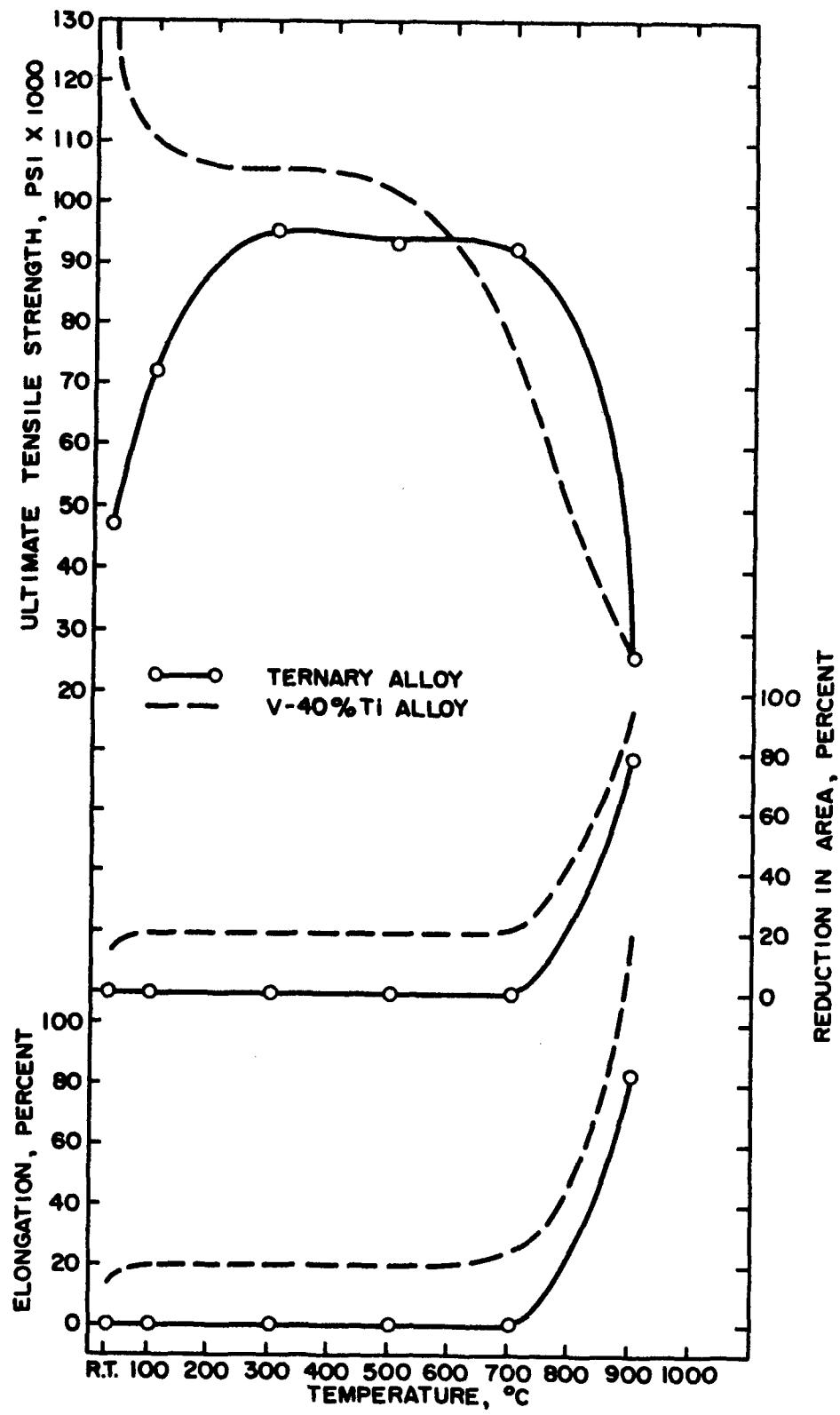
FIG. 8—ELEVATED TEMPERATURE TENSILE PROPERTIES
OF A V-40%Ti—10%Al ALLOY.

TABLE IX

ELEVATED TEMPERATURE TENSILE PROPERTIES OF V-50% Ti-5% Cr ALLOYS

WITH VARIOUS CARBON ADDITIONS (NOMINAL COMPOSITION)

Temperature °C	Hot Tensile Data, Ultimate Tensile Strength (% Elongation, % R.A.)			
	No Carbon	0.5%	1% C	1.5% C
R.T.	130,000 (9.4, 9.6)	121,200 (15.6, 28.7)	124,000 (16.5, 33.7)	125,000 (4.0, 7.6)
100	121,200 (17.2, 13.5)	117,000 (18.7, 47.2)	-	-
300	118,800 (15.6, 15.5)	115,400 (15.6, 37.1)	-	-
500	105,200 (7.8, 4.0)	119,200 (21.9, 39.7)	114,900 (26.0, 36.9) 113,600 (16.5, 17.3)	116,000 (14.0, 26.5)
700	66,200 (17.2, 7.2)	85,000 (12.5, 17.5)	-	116,000 (9.6, 26.5)
750	-	-	47,400 (45.0, 65.9)	-
900	28,200 (135, >95)	23,000 (165.7, >95)	-	-

TABLE X

ELEVATED TEMPERATURE TENSILE PROPERTIES

OF A V-50% Ti-10% Cr-0.5% C (NOMINAL COMPOSITION) ALLOY

Temperature °C	Ultimate Tensile Strength psi	Elongation %	R.A. %
500	121,600 (111,000)	14.0 (7.8)	20.1 (7.5)
700	68,200 (82,900)	21.0 (4.2)	22.3 (7.0)

Data in brackets refer to the same alloy without the carbon addition.

TABLE XI

ELEVATED TEMPERATURE TENSILE PROPERTIES

OF A V-50% Ti-15% Cr-0.5% C (NOMINAL COMPOSITION) ALLOY

Temperature °C	Ultimate Tensile Strength psi	Elongation %	R.A. %
R.T.	151,200* (145,800)	>9.0 (1.5)	21.7 (0)
500	133,000 (137,300)	20.0 (12.0)	29.7 (23.1)
700	78,200 (80,200)	4.5 (0)	6.2 (0)

Data in brackets refer to the same alloy without the carbon addition.

* Fractured at the shoulder.

TABLE XII

ELEVATED TEMPERATURE TENSILE PROPERTIES OF V-40% Ti-5% Cr ALLOYS

WITH VARIOUS CARBON ADDITIONS (NOMINAL COMPOSITION)

Temperature °C	Hot Tensile Data, Ultimate Tensile Strength (% Elongation, % R.A.)		
	No Carbon	0.5% C	1% C
500	115,800 (21.9, 175)	113,800 (5.0, 10.0)	122,900 (16.0, 20.9)
700	90,200 (14.1, 8.8)	40,000 (66.0, 85.7)	91,200 (18.5, 32.3)

TABLE XIII

ELEVATED TEMPERATURE TENSILE PROPERTIES

OF A V-40% Ti-5% Al-0.5%C (NOMINAL COMPOSITION) ALLOY

Temperature °C	Ultimate Tensile Strength psi	Elongation %	R.A. %
R.T.	138,400 (134,600)	13.0 (23.4)	33.7 (25.8)
100	125,600* (122, 200)	8.0* (17.2)	10.0* (29.3)
300	124, 400* (115,600)	9.0* (15.6)	10.6* (30.5)
500	132,800 (109,600)	18.5 (9.4)	23.1 (19.5)
600	118,800* (-)	9.5* (-)	11.5* (-)
700	89,000 (96,600)	15.0 (9.4)	21.7 (16.7)
900	29,200 (35,200)	119.0 (28.2)	98.6 (25.2)

Data in brackets refer to the same alloy without the carbon addition.

* Bad forging defect.

TABLE XIV

ELEVATED TEMPERATURE TENSILE PROPERTIES

OF A V-50% Ti-10% Al-0.5% C (NOMINAL COMPOSITION) ALLOY

Temperature °C	Ultimate Tensile Strength psi	Elongation %	R.A. %
R.T.	123,200* (84,000)	- (0)	- (0)
500	116,200 (107,400)	1.0 (3.6)	1.4 (0.7)
600	126,200 (-)	6.0 (-)	12.5 (-)

Data in brackets refer to the same alloy without the carbon addition.

* Fractured at a shoulder.
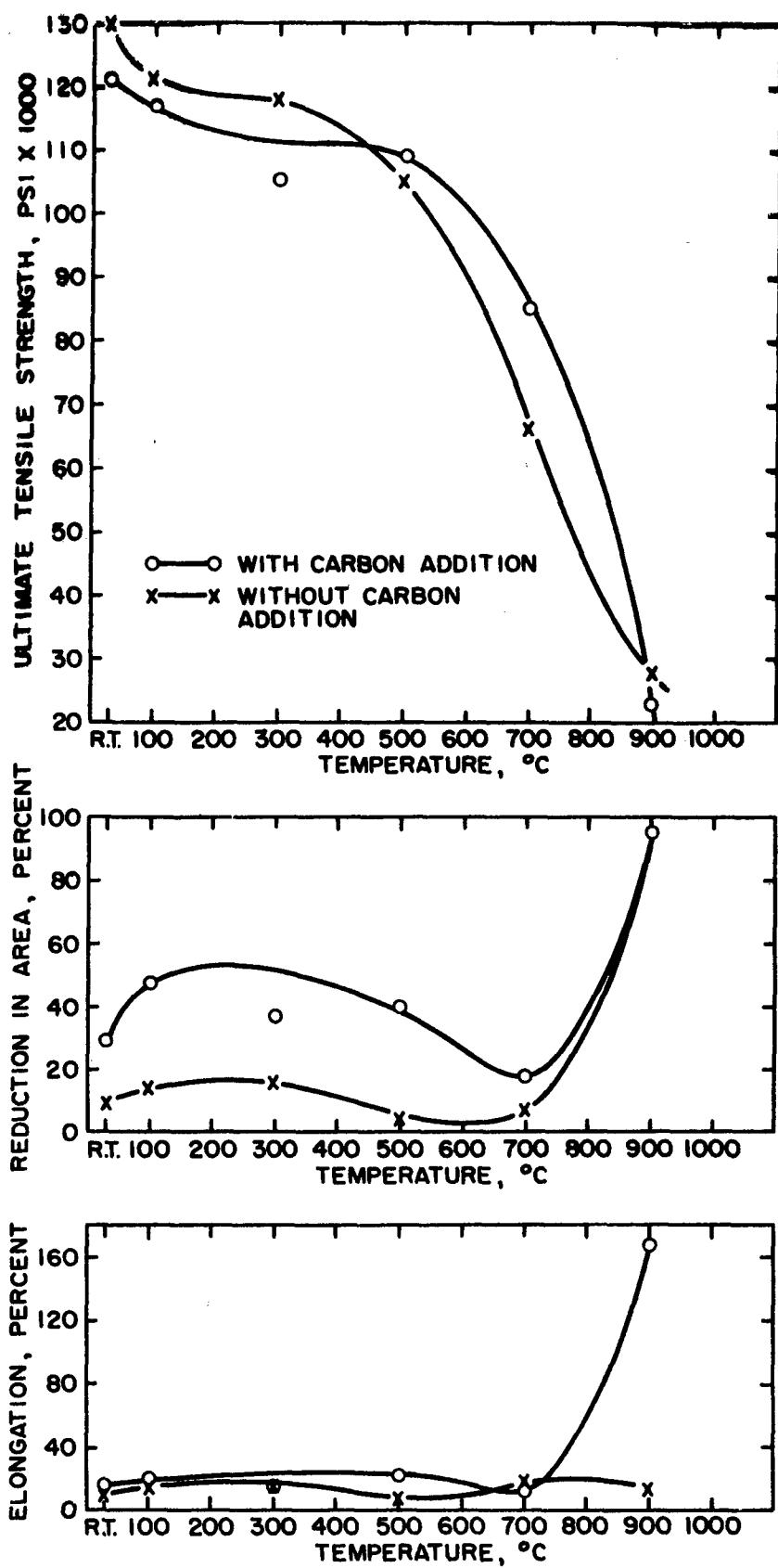
FIG. 9—ELEVATED TEMPERATURE TENSILE PROPERTIES
OF V-50%Ti-5%Cr-0.5%C ALLOY.
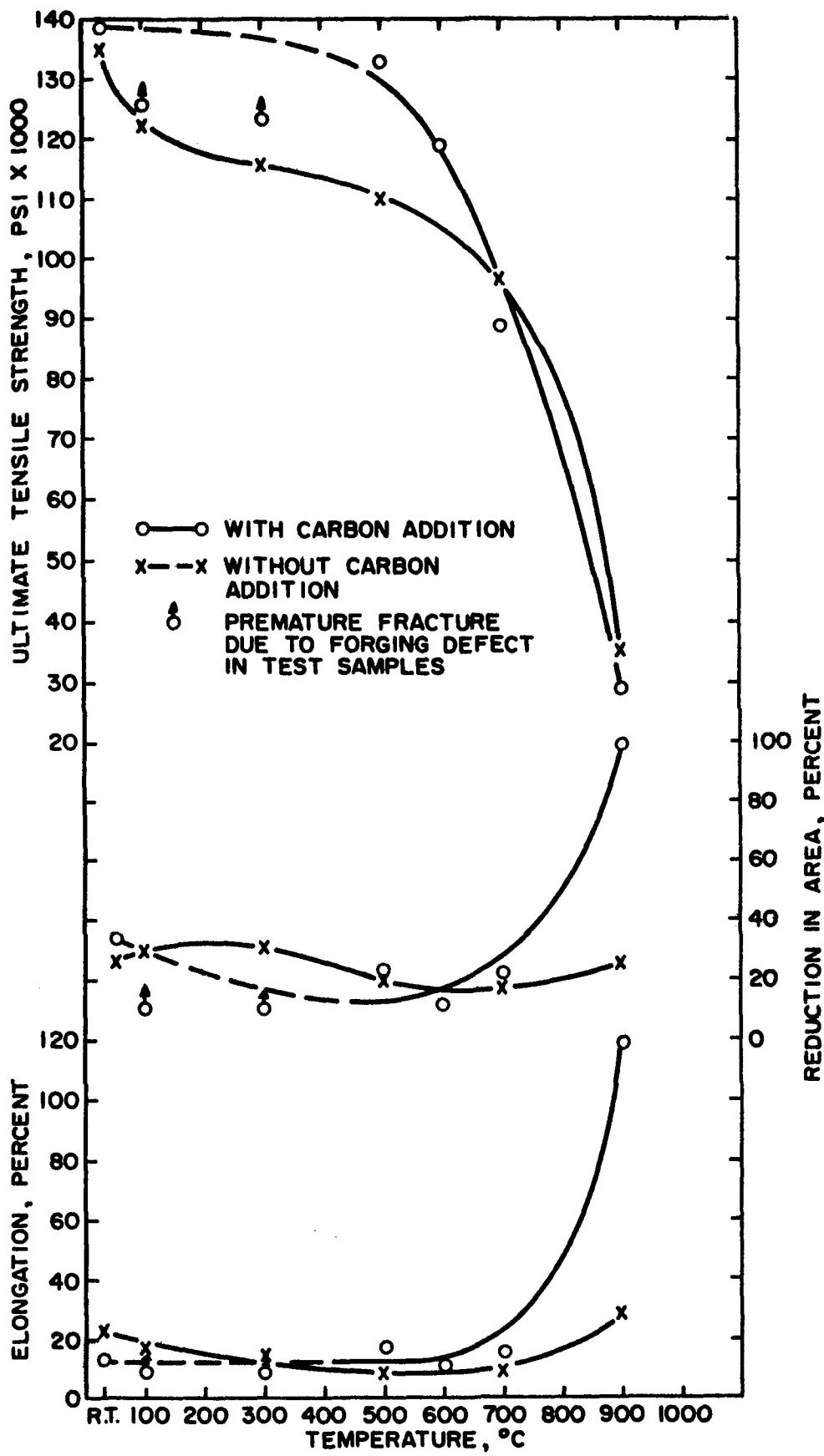
FIG. 10 – ELEVATED TEMPERATURE TENSILE PROPERTIES
OF AV-40% Ti-5% Al-0.5 % C ALLOY

(a) There is no consistent indication that the presence of free carbides influences the tensile strength of any of the alloys.

(b) Tensile ductilities of alloys containing carbon additions are generally better than the same alloys without carbon. There are some singular instances of remarkable superiority. The nature of the improvement in ductility through carbon additions is something of a puzzle. The effect on the as-cast structure can be readily rationalized but the tensile test work was done on alloys which had been hot worked beyond any residual cast structure. One is forced to believe that the presence of carbon acts in some constitutional fashion to reduce the contents of other interstitial elements (O,N) in solid solution.

4.   Tensile Properties of V-Ti-Al Alloys Made From Alumino-Thermic Vanadium

Ternary alloys were prepared by melting alumino-thermic vanadium (containing ~13% aluminum) with sponge titanium. The ratio of vanadium to aluminum was therefore fixed. A number of these alloys proved unforgeable without the benefit of carbon additions. Accordingly the influence of carbon content on each of the basic ternary compositions was investigated. The following alloys were included in this program:

$$V + 45\% \text{ Ti} + 7.6\% \text{ Al} + 0\text{-}1.5\% \text{ C (nominal)}$$
$$V + 50\% \text{ Ti} + 6.9\% \text{ Al} + 0\text{-}1.5\% \text{ C (nominal)}$$
$$V + 55\% \text{ Ti} + 6.2\% \text{ Al} + 0\text{-}1.5\% \text{ C (nominal)}$$
$$V + 60\% \text{ Ti} + 5.5\% \text{ Al} + 0\text{-}1.5\% \text{ C (nominal)}$$
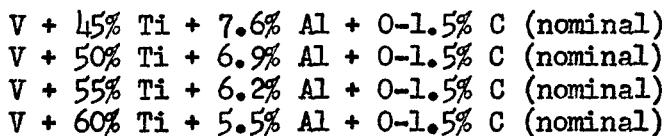
Tensile properties at room temperature, 500° and 700°C, respectively, are summarized in Table XV, XVI and XVII. Examination of the data leads to the following observations:

(a) There is a continuous decrease in tensile strength at all temperatures with increasing titanium content. The same trend is obtained in the binary V-Ti alloys.

(b) By interpolation of results with ternary V-Ti-Al alloys produced from calcium-reduced vanadium, it appears that alloys based on alumino-thermic vanadium offer high tensile strengths at room temperature and at 500°C. At 700°C, the reverse is true. The lower temperature strength superiority is probably due to the higher content of interstitial elements - 0.32% O + N + C for alumino-thermic vanadium as compared with 0.17% for calcium reduced vanadium.

(c) The V + 50% Ti + 6.9% Al and V + 45% Ti + 7.6% Al alloys based on alumino-thermic vanadium were unforgeable. Carbon additions were necessary to impart forgeability. The analagous ternary alloys based on calcium reduced vanadium permitted forging with aluminum contents as high as 10%.

(d) Additions of up to 1.2% carbon were made on certain alloys but only at 700°C is there any obvious effect of increase in strength with carbon content. At room temperature and at 500°C tensile strength is

TABLE XV

ROOM TEMPERATURE TENSILE PROPERTIES OF ALUMINO-THERMIC VANADIUM ALLOYS

WITH VARIOUS TITANIUM, ALUMINUM AND CARBON CONTENTS

Alloys	Ultimate Tensile Strength psi	Elongation %	Reduction in Area %	Analyzed C Content %
V-60% Ti-5.6% Al	131,400	9.9	26.5	-
V-60% Ti-5.5% Al-0.5% C	129,800	12.1	27.7	0.15
V-60% Ti-5.5% Al-1% C	132,000	11.0	24.3	0.21
V-60% Ti-5.4% Al-1.5% C	131,000	9.6	17.3	0.40
V-55% Ti-6.3% Al	137,600	11.2	32.3	-
V-55% Ti-6.2% Al-0.5% C	139,200	9.8	13.7	0.25
V-55% Ti-6.2% Al-1% C	143,200	11.1	29.1	0.80
V-55% Ti-6.1% Al -1.5% C	143,200	5.0	7.6	1.14 (M)
V-50% Ti-6.9% Al-0.5% C	142,600	13.4	31.1	0.41
V-50% Ti-6.9% Al-1% C	144,600	9.0	6.8	1.17 (M*)
V-50% Ti-6.8% Al-1.5% C	142,400	2.0	6.2	0.33
	132,800	2.0	1.4	1.13
V-45% Ti-7.6% Al-0.5% C	154,400	8.0	9.2	0.17
V-45% Ti-7.6% Al-1% C	162,800	11.0	20.1	0.34
V-45% Ti-7.5% Al-1.5% C	133,200	0	0	0.32

* Forging Seam
(M) Vanadium-carbon master alloy (20% carbon) used.

TABLE XVI

TENSILE PROPERTIES AT 500°C OF ALUMINO-THERMIC VANADIUM ALLOYS

WITH VARIOUS TITANIUM, ALUMINUM AND CARBON CONTENTS

Alloys	Ultimate Tensile Strength psi	Elongation %	Reduction in Area %
V-60% Ti-5.5% Al-0.5% C	116,000	19.0	34.9
V-60% Ti-5.5% Al-1% C	118,600	17.5	30.5
V-60% Ti-5.4% Al-1.5% C	115,600	8.0	14.5
V-55% Ti-6.2% Al-0.5% C	116,800	18.5	28.5
V-55% Ti-6.2% Al-0.5% C	128,600	18.0	30.4 (M)
V-55% Ti-6.2% Al-1% C	124,200	18.5	31.9
V-55% Ti-6.2% Al-1% C	125,800	7.5	11.3 (M*)
V-55% Ti-6.1% Al-1.5% C	131,800	15.0	22.5
V-50% Ti-6.9% Al-0.5% C	128,800	31.0	24.3
V-50% Ti-6.9% Al-1% C	136,200	11.0	15.3 (M+)
V-50% Ti-6.8% Al-1.5% C	131,800	16.0	21.7
V-50% Ti-6.8% Al-1.5% C	131,400	3.5	7.8 (M*)

(M) Vanadium-carbon master alloy (20% carbon) used.

* Unmelted carbon master alloy observed in the fracture.

+ Forging seam.

TABLE XVII

TENSILE PROPERTIES AT 700°C OF ALUMINO-THERMIC VANADIUM ALLOYS

WITH VARIOUS TITANIUM, ALUMINUM AND CARBON CONTENTS

Alloys	Ultimate Tensile Strength psi	Elongation %	Reduction in Area %	Analyzed C Content %
V-60% Ti-5.6% Al	44,400	48.3	93.6	-
V-60% Ti-5.5% Al-0.5% C	37,600	49.2	84.5	0.15
V-60% Ti-5.5% Al-1% C	40,600	43.3	84.5	0.52
V-60% Ti-5.4% Al-1.5% C	59,000	20.7	41.4	0.40
V-55% Ti-6.3% Al	55,600	42.5	89.2	-
V-55% Ti-6.2% Al-0.5% C	48,100	56.8	86.1	0.25
V-55% Ti-6.2% Al-0.5% C	58,800	66.5	74.9	0.44 (M)
V-55% Ti-6.2% Al-1% C	55,800	40.9	79.1	0.80*
V-55% Ti-6.2% Al-1% C	63,000	43.5	73.8	0.95 (M)
V-55% Ti-6.1% Al-1.5% C	69,400	39.0	55.4	1.14 (M)
V-50% Ti-6.9% Al-0.5% C	50,200	26.6	71.7	0.41
V-50% Ti-6.9% Al-1% C	53,600	38.0	77.3	-
V-50% Ti-6.9% Al-1% C	72,000	32.0	52.0	0.63 (M)
V-50% Ti-6.8% Al-1.5% C	76,600	23.7	61.6	0.93

(M) Vanadium-carbon master alloy used.

* Forging seam.

substantially independent of carbon content. Ductilities, however, appear
to be reduced at higher carbon levels. It appears therefore that carbon
is a desirable addition as a general safeguard of forgeability but that it
confers little advantage in terms of improved tensile properties.

(e) The tensile behavior of alloys based on alumino-thermic
vanadium when rendered satisfactorily forgeable by carbon additions are
as good as or superior to the same alloys produced from the purer and
considerably more expensive calcium-reduced vanadium.

VI. STRESS-RUPTURE BEHAVIOR OF VANADIUM ALLOYS

From the elevated temperature tensile results, the most obvious
potential usefulness of vanadium alloys seemed to be in applications where
high creep strength to density is a governing design parameter. The
fundamentally lower densities of vanadium and titanium alloys place these
in the forefront of the new alloy development picture. Such titanium alloys
as Ti + 6% Al + 4% V are currently regarded as superior to anything else in
the temperature range 350°-550°C on a creep strength to density basis of
comparison.

The program of stress-rupture testing was initiated before the final
conclusion on possible retardation of oxidation rates had been arrived at.
The majority of the alloy compositions was therefore selected on the basis
of apparently superior oxidation resistance and high tensile strength on
short time testing. In the light of the decision that serious oxidation
cannot be satisfactorily suppressed by alloying, the scope of potentially
high creep strength alloy compositions is considerably broadened.

A list of the alloys tested and the temperatures of testing are as
follows:

$$V-50\% \text{ Ti}-5\% \text{ Cr} \quad (500°, 600°, 700°C)$$
$$V-50\% \text{ Ti}-10\% \text{ Cr} \quad (500°, 600°, 700°C)$$
$$V-50\% \text{ Ti}-15\% \text{ Cr} \quad (500°, 600°, 700°C)$$
$$V-50\% \text{ Ti}-5\% \text{ Al} \quad (500°, 600°C)$$
$$V-50\% \text{ Ti}-10\% \text{ Al} \quad (500°, 600°C)$$
$$V-40\% \text{ Ti}-5\% \text{ Al} \quad (500°, 600°, 700°C)$$
$$V-50\% \text{ Ti}-5\% \text{ Cr}-0.5\% \text{ C} \quad (500°, 600°C)$$
$$V-50\% \text{ Ti}-5\% \text{ Al}-0.5\% \text{ C} \quad (500°, 600°C)$$
$$V-40\% \text{ Ti}-5\% \text{ Al}-0.5\% \text{ C} \quad (500°, 600°C)$$
$$V-50\% \text{ Ti}-6.9\% \text{ Al}-0.5\% \text{ C} \quad (600°C)$$
$$V-50\% \text{ Ti}-6.8\% \text{ Al}-1.5\% \text{ C} \quad (600°C)$$
$$V-55\% \text{ Ti}-6.2\% \text{ Al}-0.5\% \text{ C} \quad (500°, 600°C)$$
$$V-55\% \text{ Ti}-6.2\% \text{ Al}-1.0\% \text{ C} \quad (600°C)$$
$$V-60\% \text{ To}-5.5\% \text{ Al}-0.5\% \text{ C} \quad (600°C)$$

All tests were conducted in air. The test results are graphically presented in the series Figures 11 to 24. The 0.1 hour points refer to the hot tensile strength data of Section V. In all but a few instances, the time-stress dependency of rupture at any given temperature could be represented by a straight line.

A review of these test results indicates the following trends:

(a) The stress-rupture limits are sharply dependent on temperature. This can be more easily appreciated from Figure 25 which illustrates for a characteristic selection of alloys the temperature dependence of the stress for 100 hour rupture. It will be noted that there is a general tendency for curves of all the alloys to converge at about 700°C. Above that temperature level, it would appear that creep-rupture behavior is not composition dependent. There are major differences in 100 hour strength at 500°C among the alloys. The general indications are that the stress for rupture approaches an independency from time at or below 500°C; i.e. rupture stresses approach the hot tensile strengths.

(b) Aluminum confers more creep rupture strength on a 50% V-50% Ti alloy than does chromium. The differences in behavior are more apparent at 500° and 600°C. A 10% aluminum level offers no more 100 hour strength than a 5% aluminum level.

(c) The presence of carbon as free carbides adds little or nothing to the stress-rupture strength. Although the 40% Ti-5% Al-0.5% C alloy showed the highest 100 hour strength at 500°C, its superiority over the equivalent alloy with no intentional carbon addition is only about 10,000 psi. The alloy containing 50% Ti-6.9% Al-0.5% C has almost identically the same stress-rupture curve at 600°C as the same alloy with 1.5% carbon added.

(d) The 600°C stress-rupture behavior of a 50% Ti-6.9% Al-0.5% C alloy based on alumino-thermic vanadium is identical with the limits of experimental error with the 50% Ti-5% Al-0.5% C alloy based on calcium-reduced vanadium. It appears therefore that the initial purity of the vanadium is not a crucial point at these temperature levels of testing.

(e) At 500°C, the highest stress for a 100 hour rupture condition is delivered by a vanadium alloy containing 40% Ti, 5% Al and 0.5% C. At 600°C, three alloys are tied for first place:

> 40% Ti, 5% Al, 0.5% C
> 50% Ti, 10% Al
> 50% Ti, 6.8% Al, 1.5% C (alumino-thermic vanadium)

All of the alloys exhibited ductile behavior at the testing temperatures. Table XVIII and XIX summarize ductility values at fracture for seven alloys.

In order to compare the stress-rupture properties of the V-40% Ti-5% Al-0.5% C alloy with the behavior of other high temperature-high strength alloys, representative data have been taken from various sources and
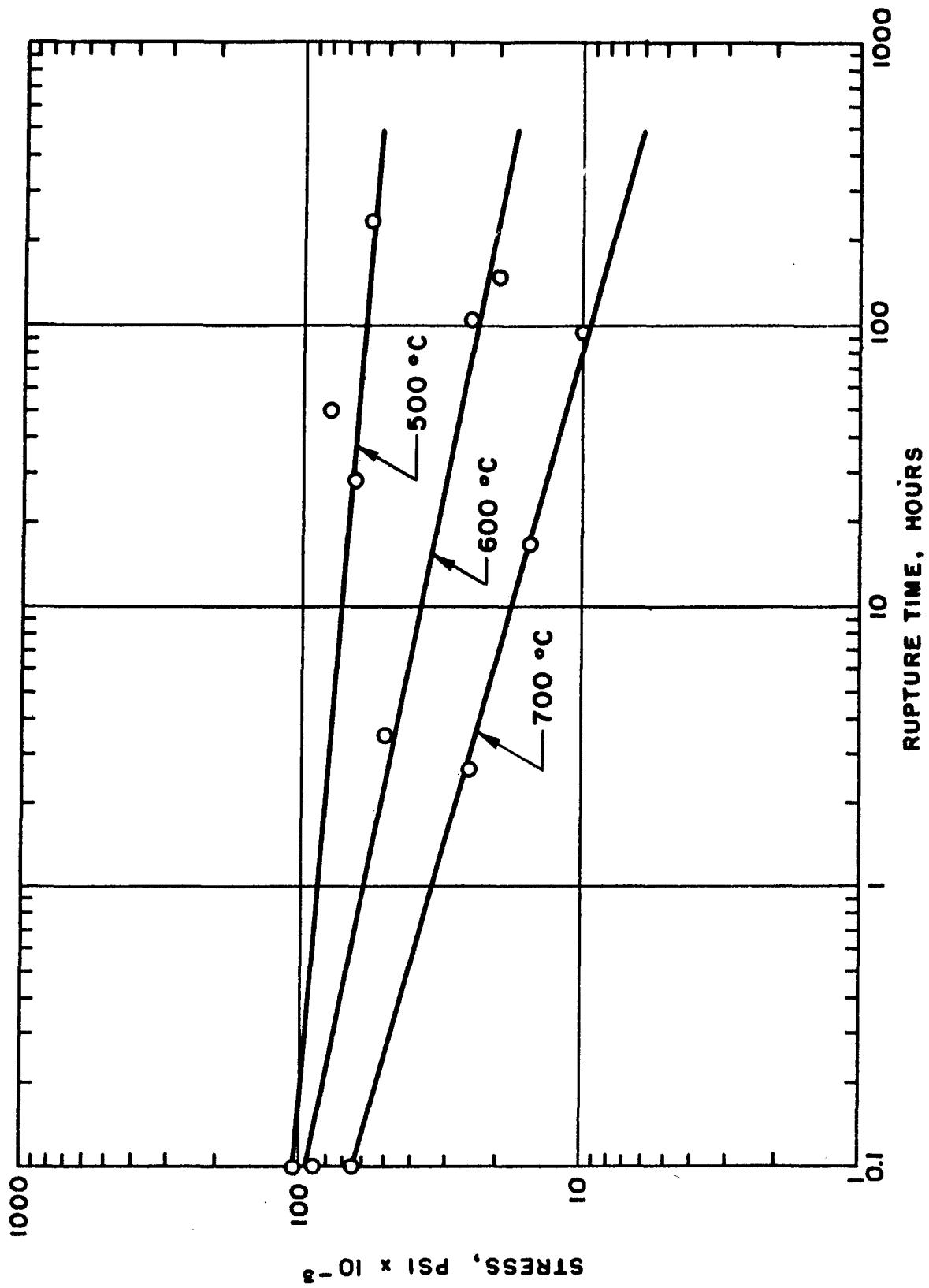
FIG. II – STRESS – RUPTURE BEHAVIOR OF A V – 50% Ti – 5% Cr ALLOY.
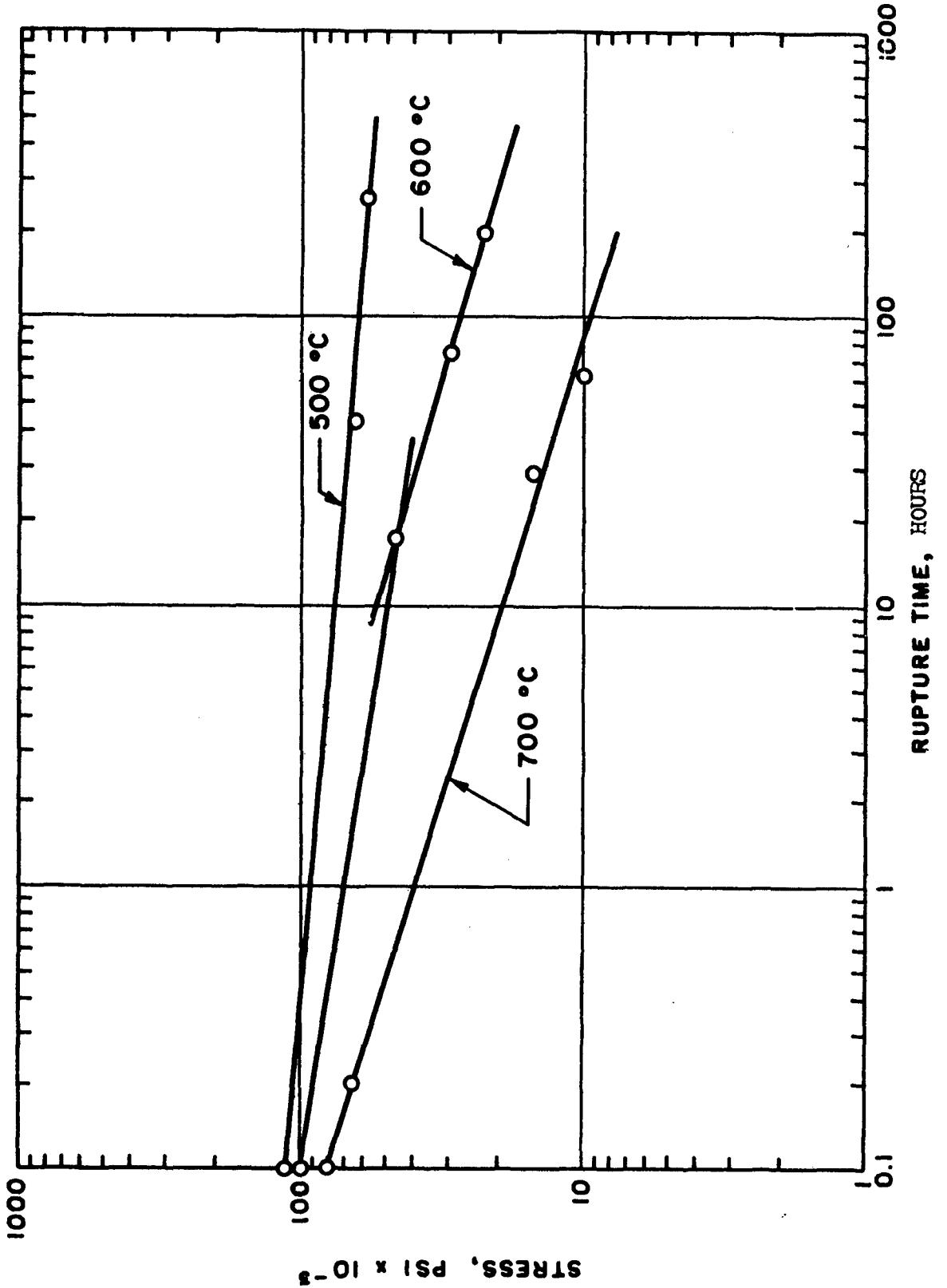
FIG.12 – STRESS – RUPTURE BEHAVIOR OF A V – 50% Ti – 10% Cr ALLOY.

FIG. 13 - STRESS - RUPTURE BEHAVIOR OF A V - 50% Ti - 15% Cr ALLOY
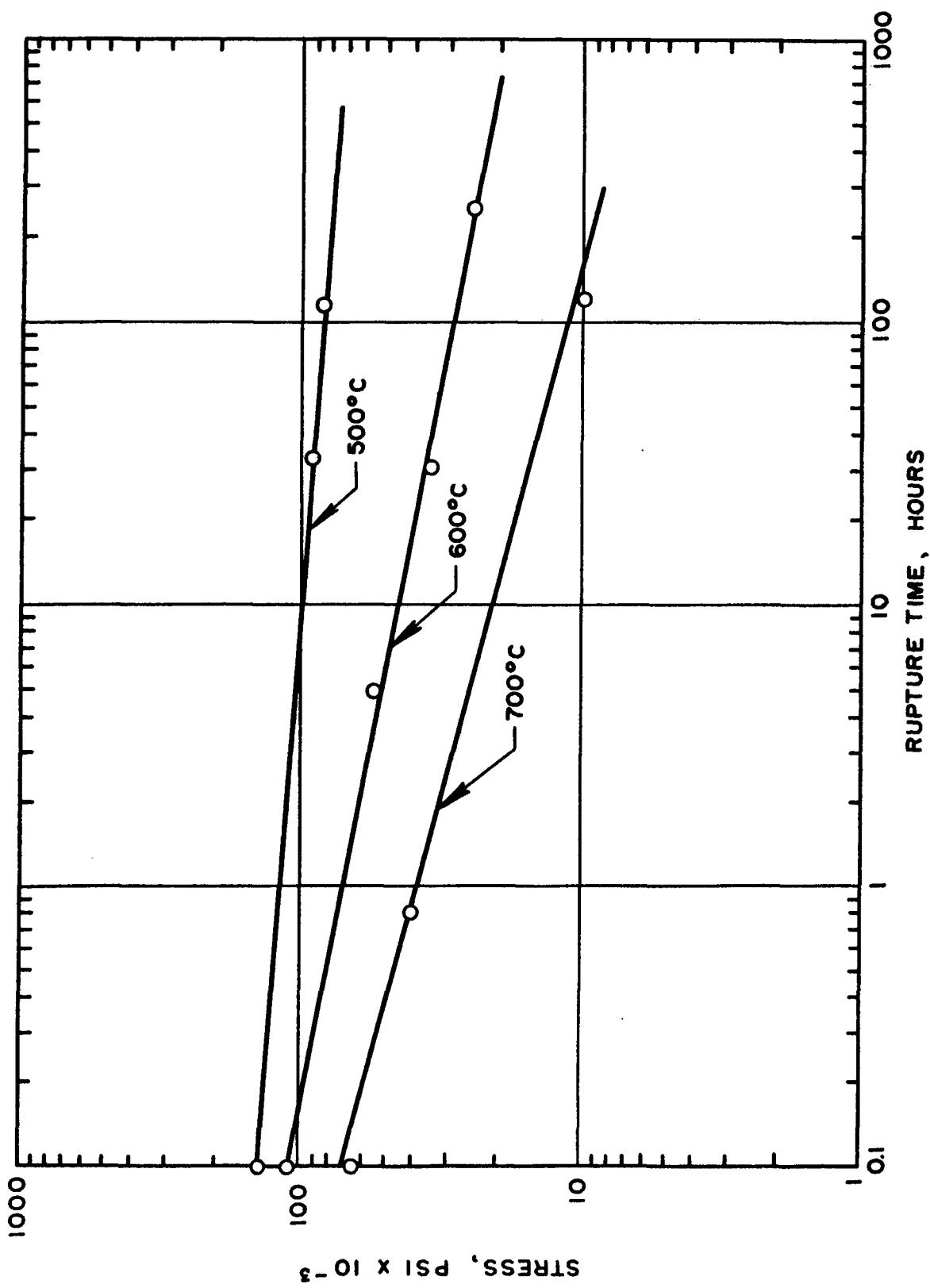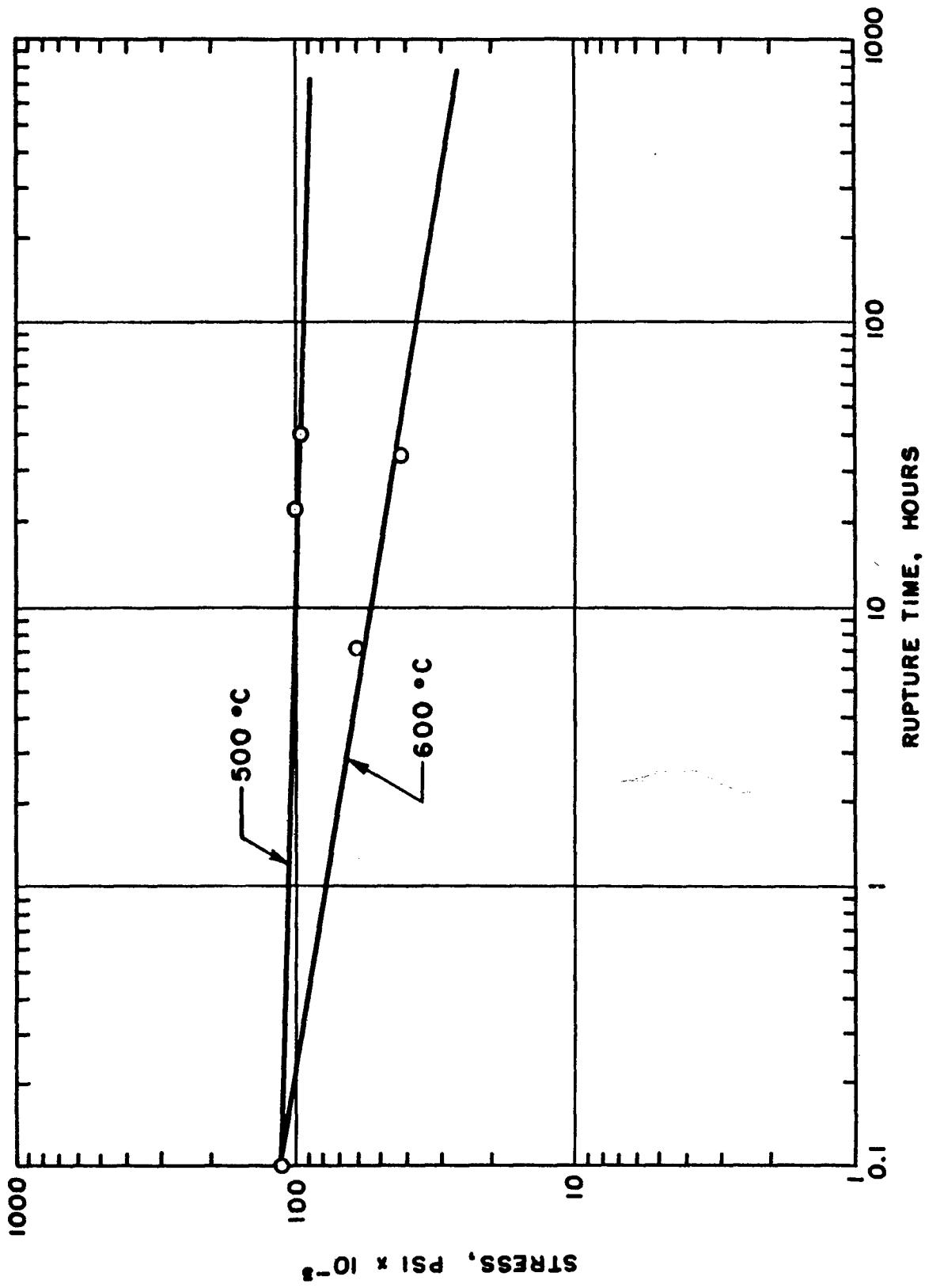
FIG. 14 — STRESS —RUPTURE BEHAVIOR OF A V – 50% Ti – 5% Al ALLOY.
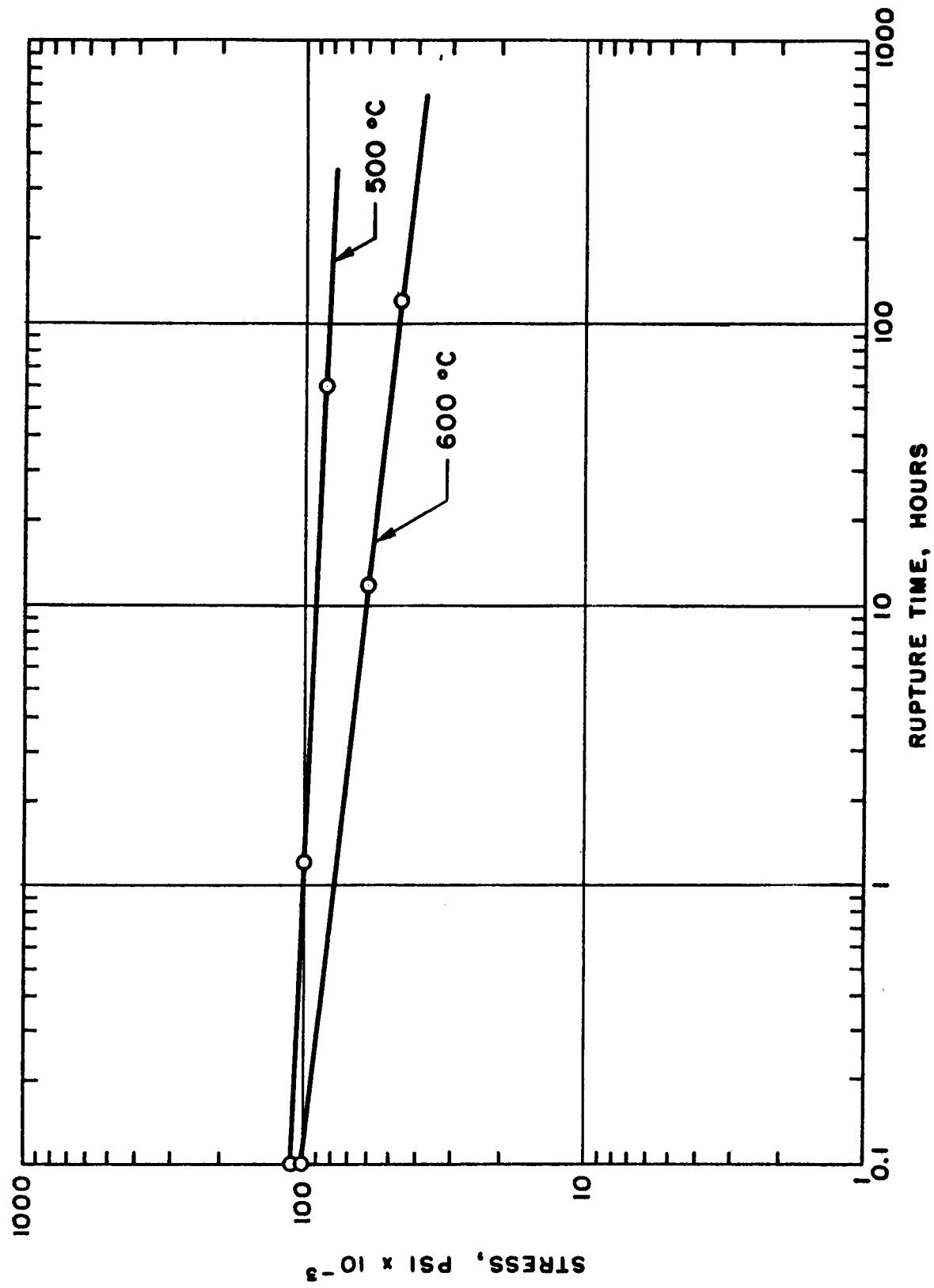
FIG. 15 - STRESS - RUPTURE BEHAVIOR OF A V-50% Ti-10% Al ALLOY.
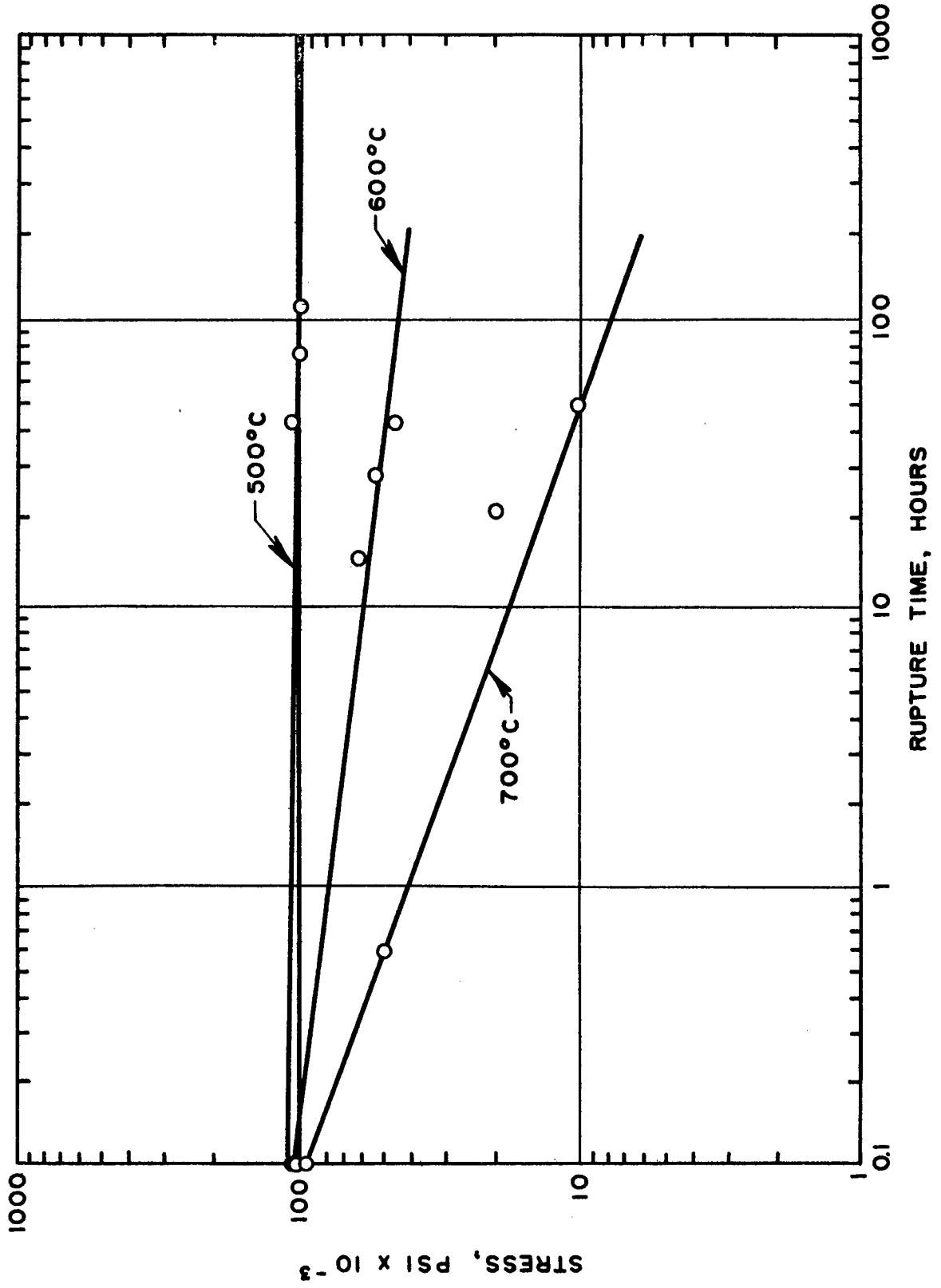
FIG. 16 - STRESS - RUPTURE BEHAVIOR OF A V - 40% Ti - 5% Al ALLOY
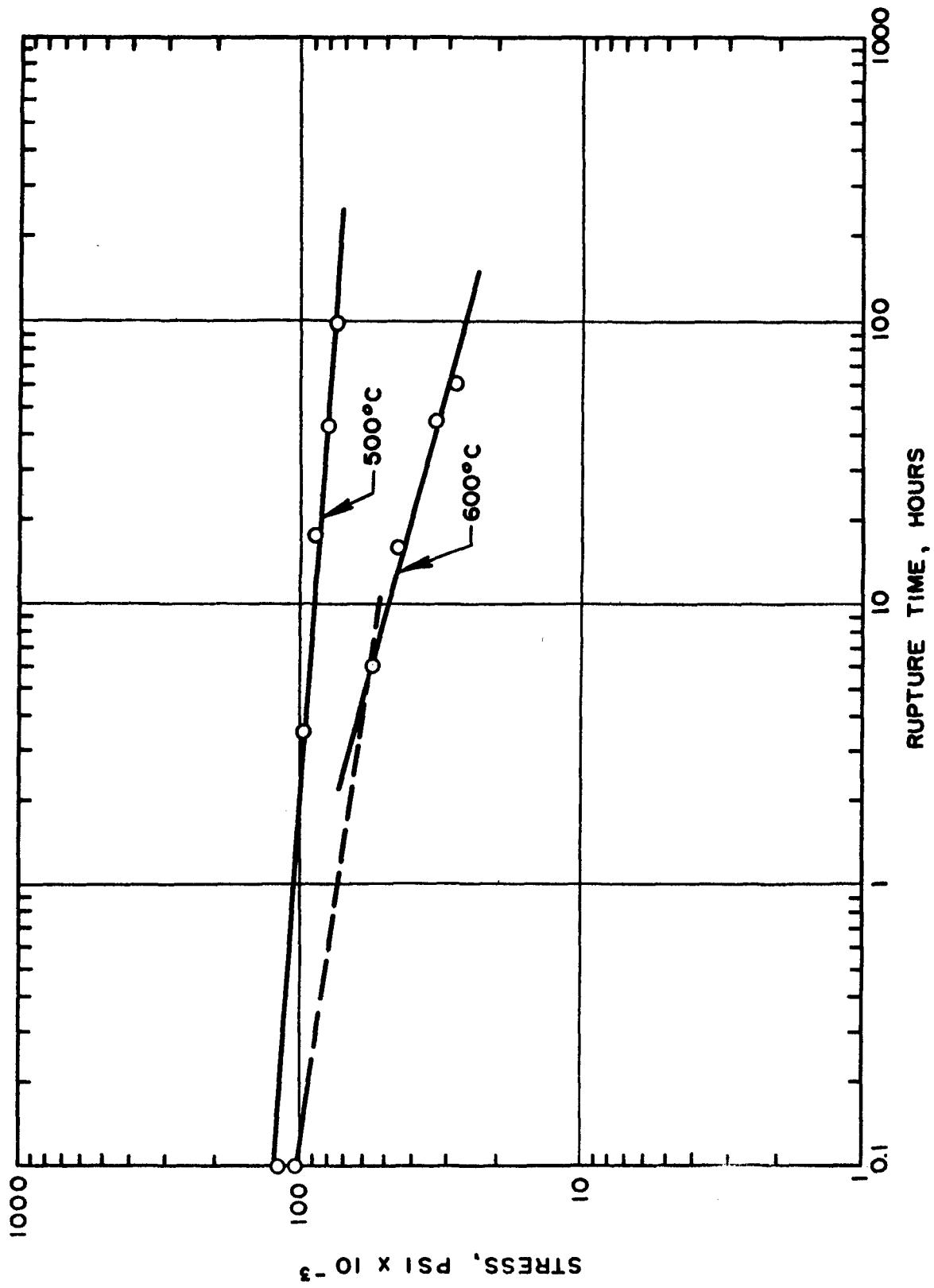
FIG. 17 - STRESS-RUPTURE BEHAVIOR OF A V-50%Ti-5% Cr-0.5%C ALLOY.
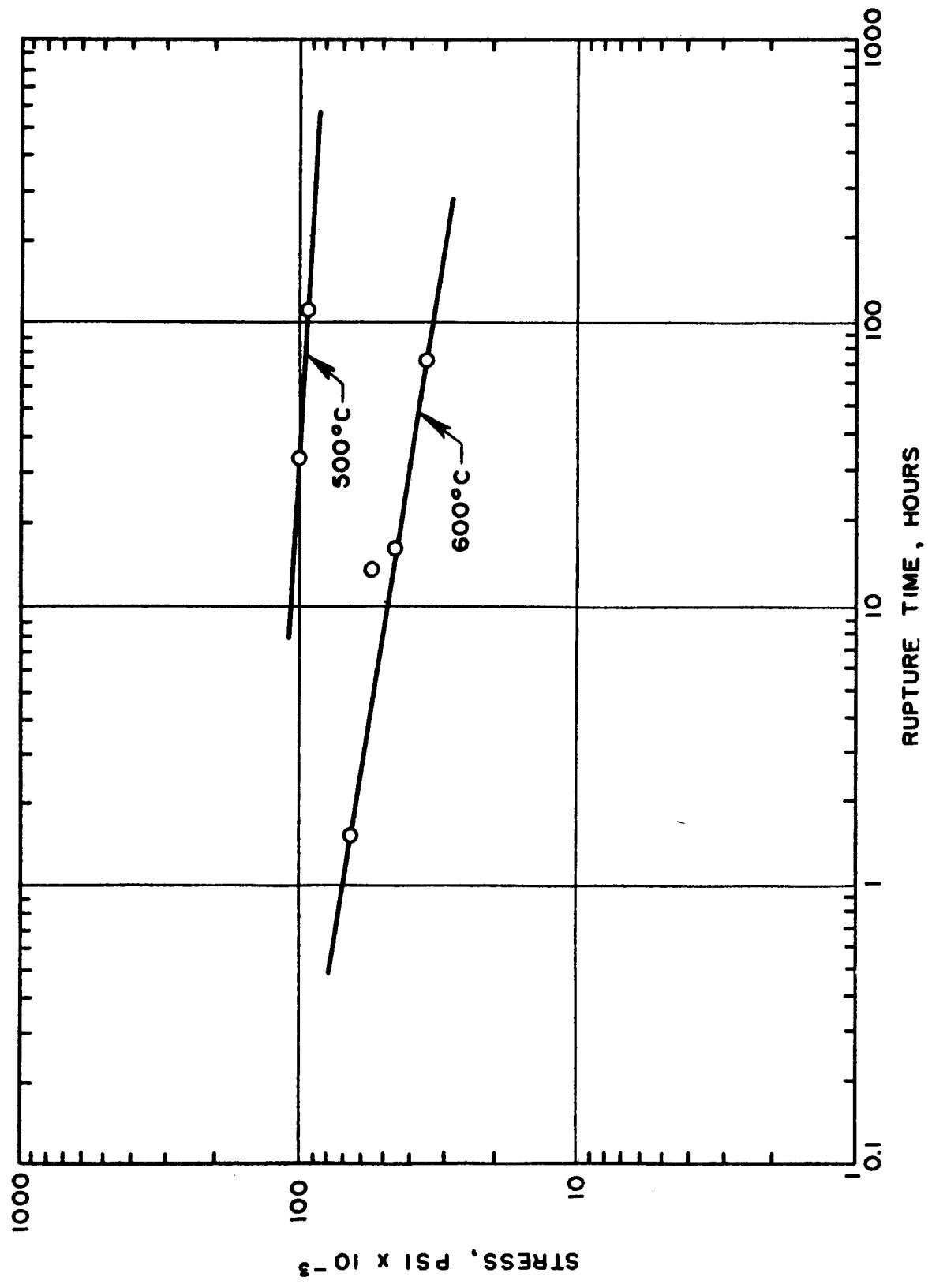
FIG. 18 - STRESS-RUPTURE BEHAVIOR OF A V-50% Ti-5% AI-0.5% C ALLOY.
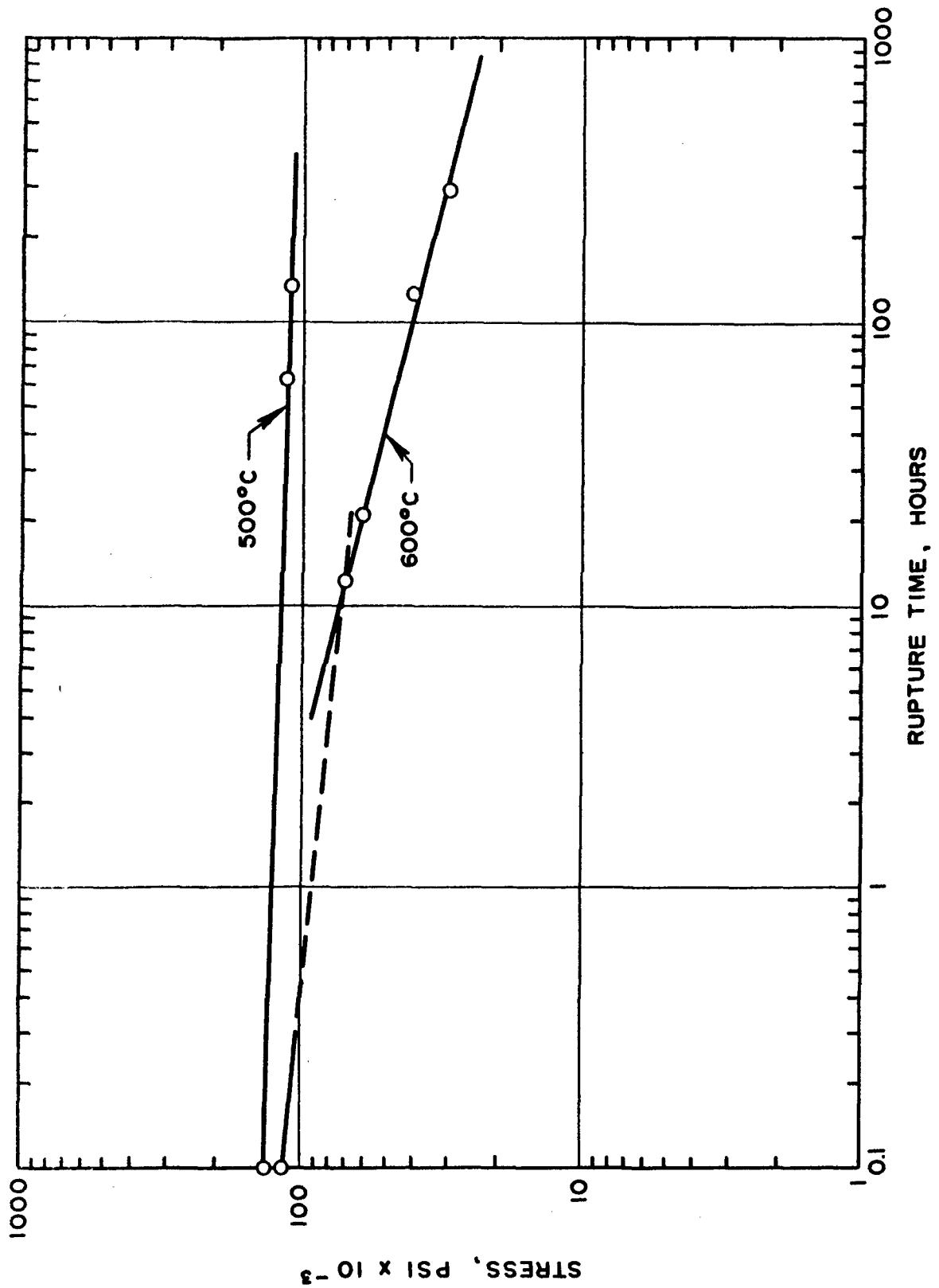
FIG. 19 – STRESS-RUPTURE BEHAVIOR OF A V – 40% Ti – 5% Al – 0.5% C ALLOY.
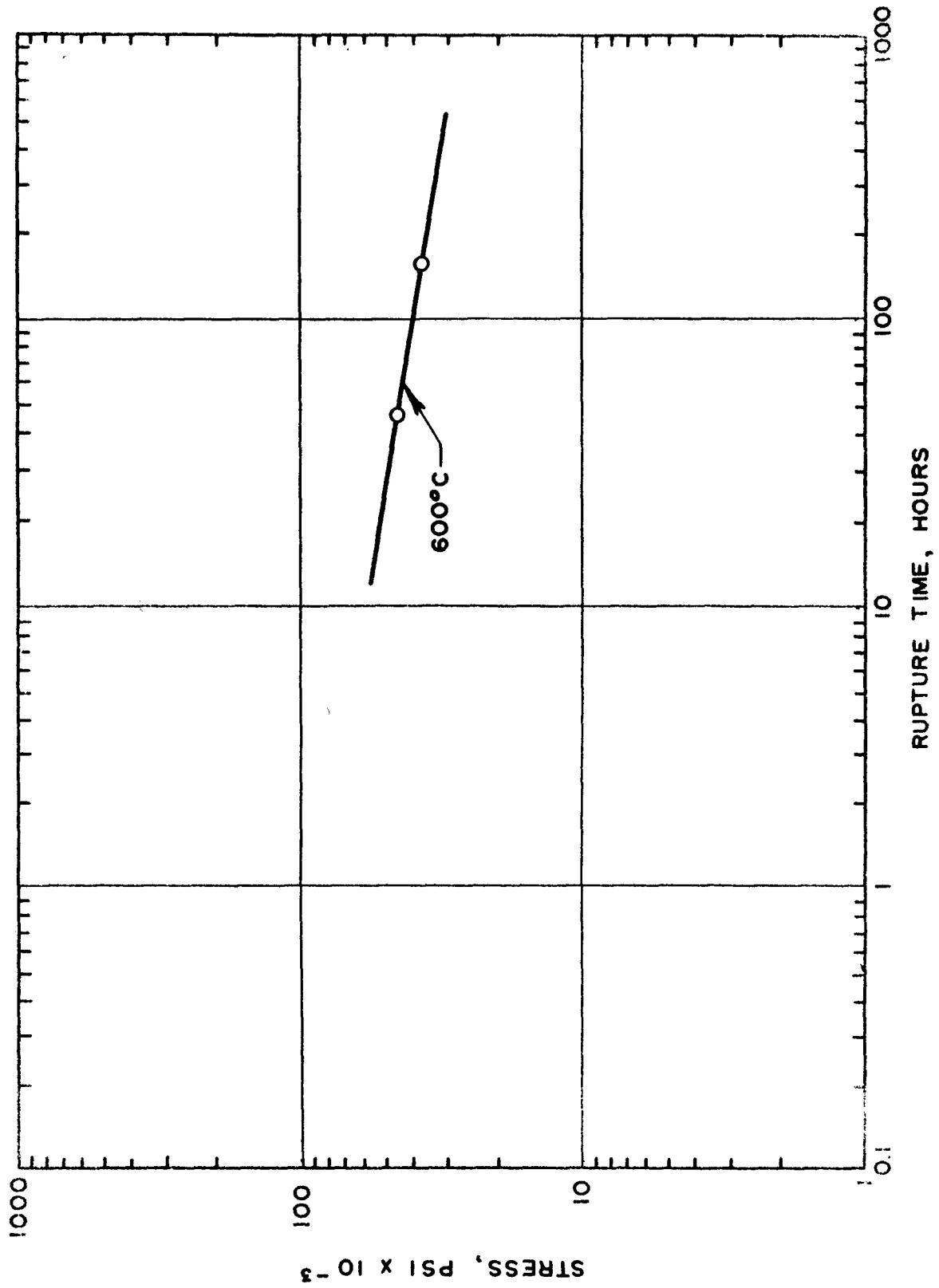
FIG 20 - STRESS-RUPTURE BEHAVIOR OF A V-50%Ti - 6.9%Al - 0.5%C ALLOY.
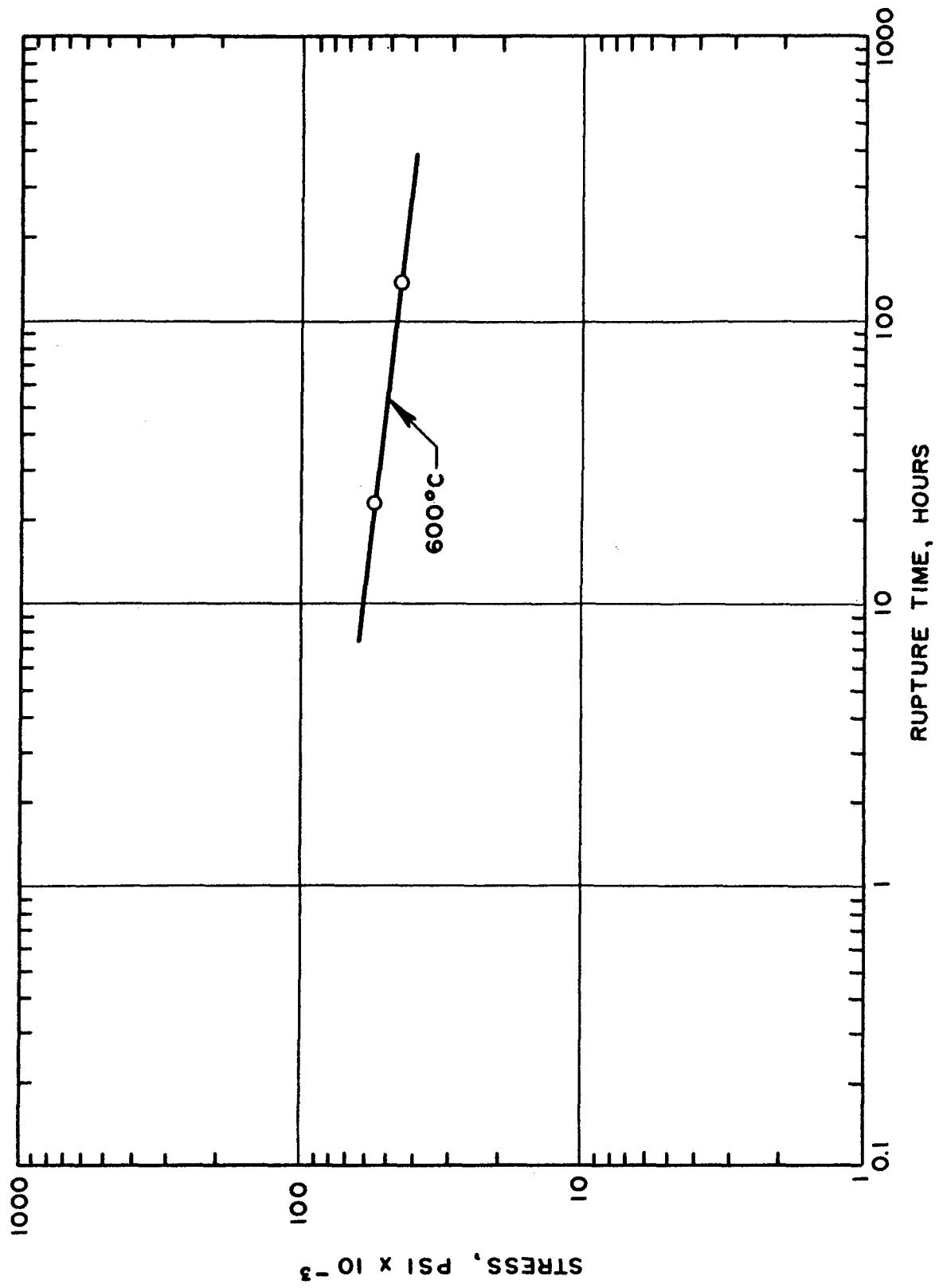
FIG. 21 – STRESS-RUPTURE BEHAVIOR OF A V–50%Ti – 6.8% AI – 1.5%C ALLOY.
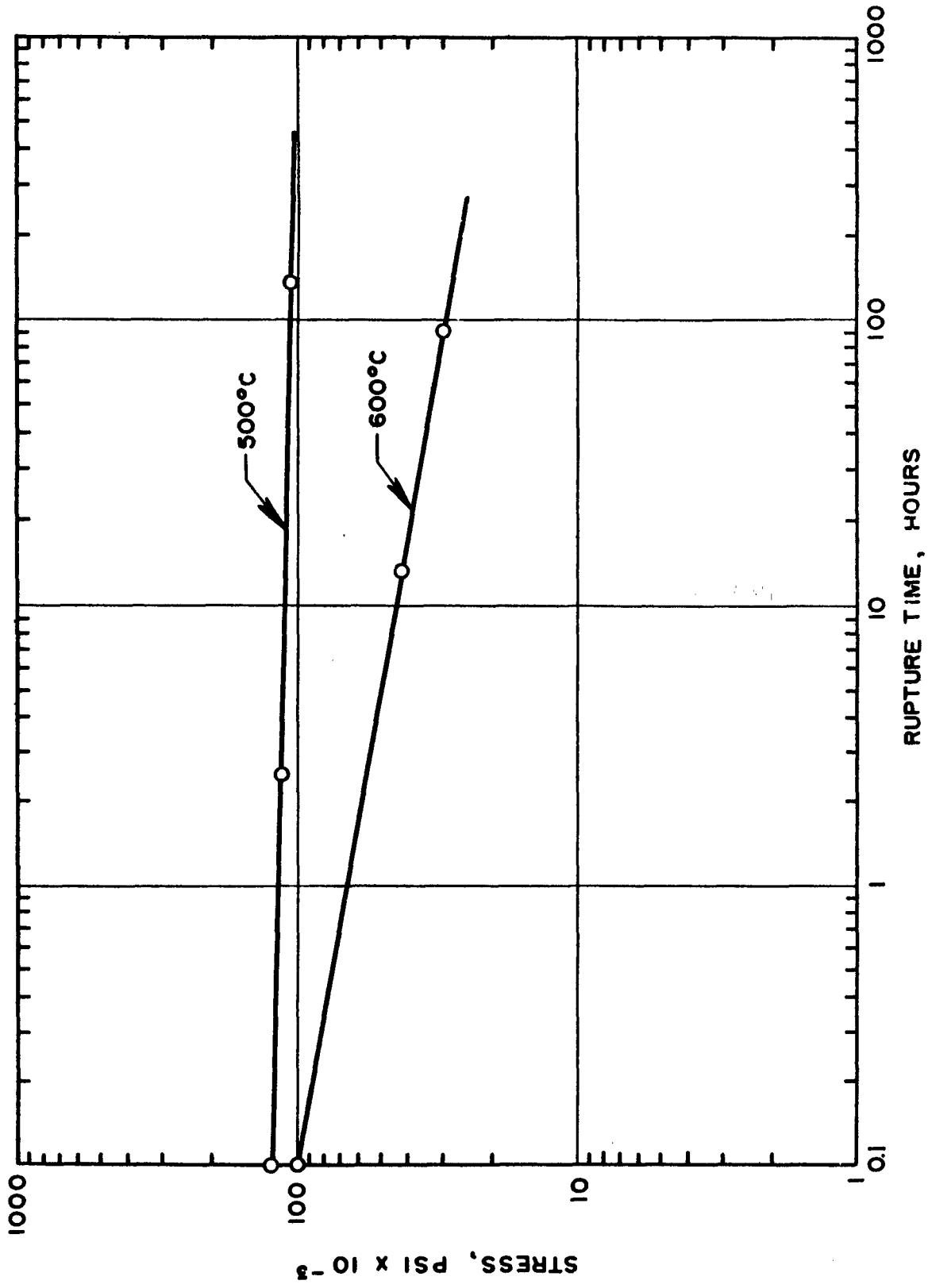
FIG. 22 - STRESS-RUPTURE BEHAVIOR OF A V - 55% Ti - 6.2% Al - 0.5% C ALLOY.
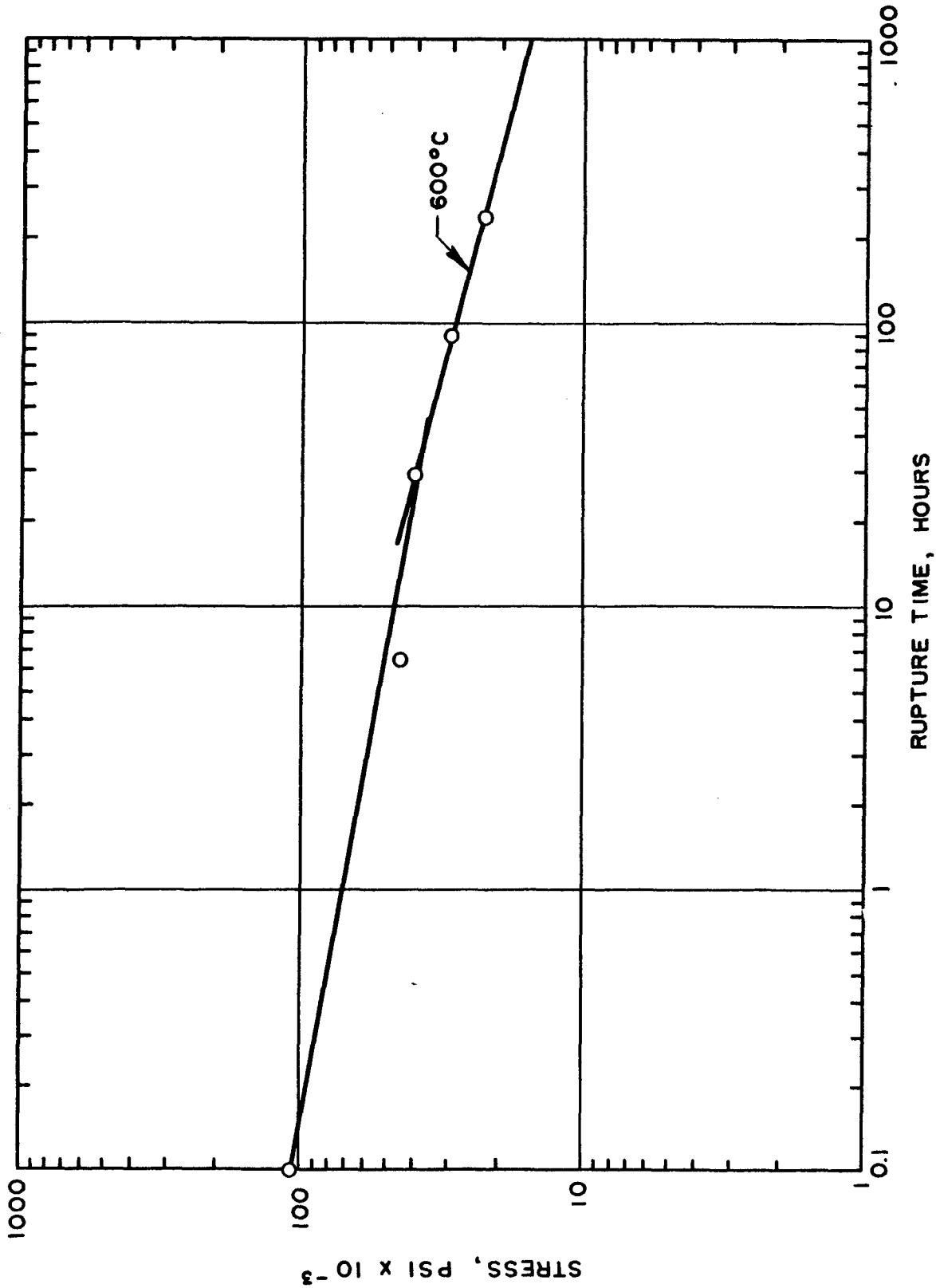
FIG. 23 – STRESS-RUPTURE BEHAVIOR OF A V-55% Ti-6.2% Al-1% C ALLOY.
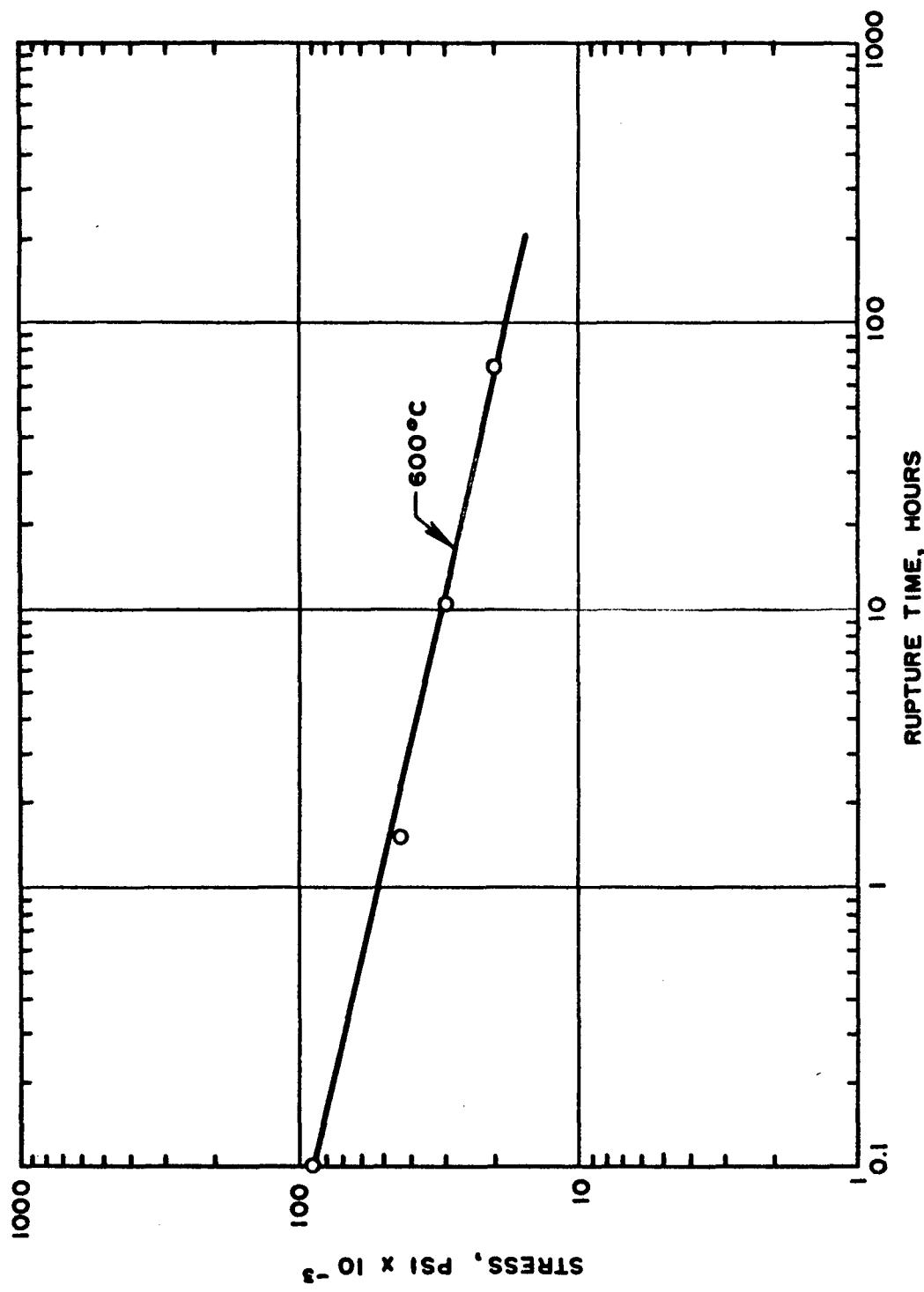
FIG. 24 - STRESS-RUPTURE BEHAVIOR OF A V-60%Ti -5.5%AI-0.5%C ALLOY.
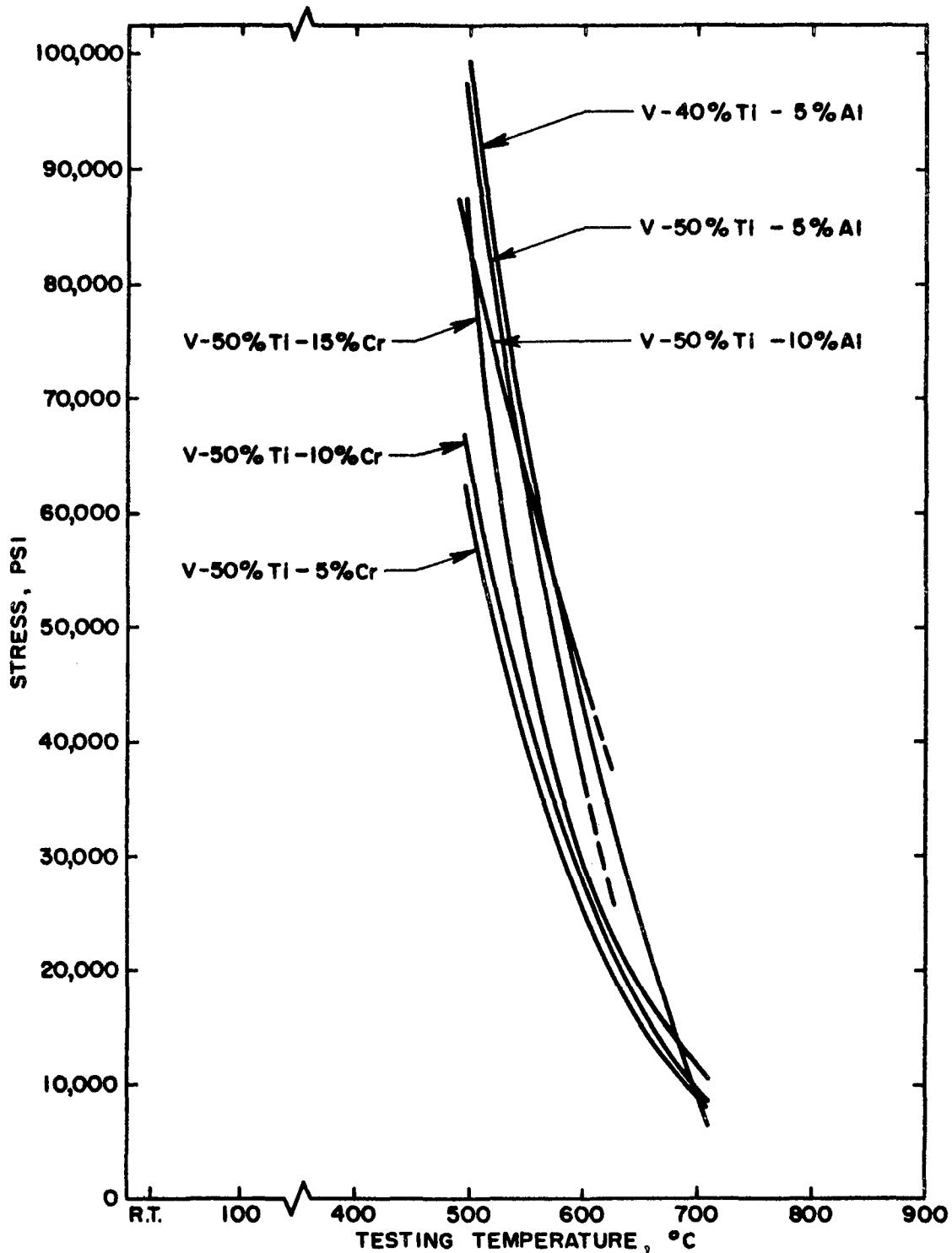
FIG. 25-100 HOUR RUPTURE LIFE OF SELECTED VANADIUM ALLOYS AS A FUNCTION OF TEMPERATURE.

TABLE XVIII

STRESS RUPTURE PROPERTIES OF V-Ti-Cr ALLOYS

Tempera-ture °C	Stress psi	Rupture Time, Hrs. - (brackets indicate % elongation)		
		V-50% Ti-15% Cr	V-50% Ti-10% Cr	V-50% Ti-5% Cr
700	65,000	0.1 (4.7%)	0.2 (17.2%)	2.6 (89.1%)
	40,000	0.8 (14.1%)		
	15,000		28.9 (106%)	16.6 (126.6%)
	10,000	120.3+ (130%)	60.6+ (145.3%)	92.3+ (97%)
600	55,000	5.0 (7.8%)		
	50,000			3.5 (37.5%)
	46,000		17.0, 16.6 (53.1, 29.7%)	
	35,000	30.5 (9.4%)		
	29,500		75.6 (34.4%)	
	25,000	250.8 (43.8%)		105.5 (76.6%)
	22,500		193.1 (137.5%)	
	20,000			148.3 (143.8%)
500	80,000			50.8 (23.4%)
	65,000		43.6 (7.8%)	28.1 (23.4%)
	59,000		259.2 (9.4%)	
	58,000			232.2 (25.0%)

TABLE XIX

STRESS RUPTURE PROPERTIES OF V-Ti-Al ALLOYS

Tempera-ture °C	Stress psi	Rupture Time, Hrs. - (brackets indicate % elongation)			
		V-40% Ti-5% Al	V-40% Ti-10% Al	V-50% Ti-5% Al	V-50% Ti-10% Al
700	50,000	0.58 (48.4%)			
	20,000	21.0 (84.4%)			
	10,000	49.7 (***)			
600	85,000	7.2 (17.2%)			
	80,000	5.1 (14.1%)			
	70,000	18.1 (23.4%)	37.3 (1.6%)**		
	62,000	14.5, 19.3 (20.3%)	*		
	60,000			7.1 (51.6%)	11.7 (14.1%)**
	53,000	28.2 (21.9%)			
	46,000	43.2 (25.0%)			121.7 (15.6%)**
	42,000			26.3 (57.8%)	
	35,000			32.6 (65.6%)	
500	107,500	56.8 (3.1%)			
	105,000	42.9 (9.4%)			
	100,000	75.6 (1.6%)	*	22.0 (29.7%)	1.2 (1.0%)
	98,000	109.0 (3.1%)			
	96,000			39.8 (20.3%)	
	90,000		*		
	85,000				60.6 (1.5%)
	80,000		*		

*   Fractured on loading.

**   Approximate values because of very heavy scale built up during tests.

***   No value was obtained since the piece was deteriorated after long hours at the temperature.

reduced by interpolation to stress-rupture values for 100 hour failure in the temperature range 500°-700°C. Titanium-, cobalt-, nickel- and iron-base alloys are represented, each being superior in its class.

The trends of behavior are illustrated in Figure 26. A "stress to cause rupture divided by density" parameter is used as an order of merit. Pertinent data and source references are summarized in Table XX. It is clear that the vanadium and titanium alloys are both considerably superior to the other three above 550°C. The vanadium alloy is as good as or slightly better than the titanium alloy which represents the best so far developed.

Time and funds did not permit more than a cursory examination of creep behavior. Data were, however, taken for two alloys and these are presented in Figure 27.

VII. SUMMARY

Three years have been spent on a study of the properties of vanadium and its alloys and means for producing them in useful form. The research program has concerned itself with melting, forging and heat treatment practice, phase equilibria, tensile properties, hardness, stress-rupture behavior and oxidation resistance. Minor diversions have been made to develop useful points of information on cold rolling, recrystallization, vanadium-oxygen phase equilibria, and electroplating.

In its unalloyed form, vanadium may be regarded a low strength, very ductile metal. Its ductility like titanium, zirconium and other high melting point transition elements is most severely limited by the content of interstitial elements -- oxygen and nitrogen -- held in solid solution. Accordingly, melting and heat treatment procedures must be designed primarily to prevent any increase in the existent level of interstitials. Because of this and because of its very high melting temperature (1900°C), vanadium and its alloys must be melted in the cold mold arc furnaces currently in use for titanium and zirconium alloys.

Rudimentary phase relationships were established for 21 vanadium-base binary systems. Such information as solubility limits, intermediate phases and transformations, by which solid solutions and intermediate phases achieved equilibrium, was obtained. It was found that 15 elements have appreciable solid solubilities in vanadium. These include: Al(34.6 wt. %), Si(5%), Ti(100%), Cr(>40%), Mn(>15%), Fe(100%), Co(23%), Ni(9%), Cu(9%), Zr(3%), Nb(100%), Mo(100%), Sn(>10%), Ta(100%), W(50%). Except in the instance of V-Ti alloys, none of the binary systems permitted forgeability beyond 10% alloy addition or beyond the solubility limit if this was a lesser value. The V-Ti alloys proved forgeable over the whole range of compositions.
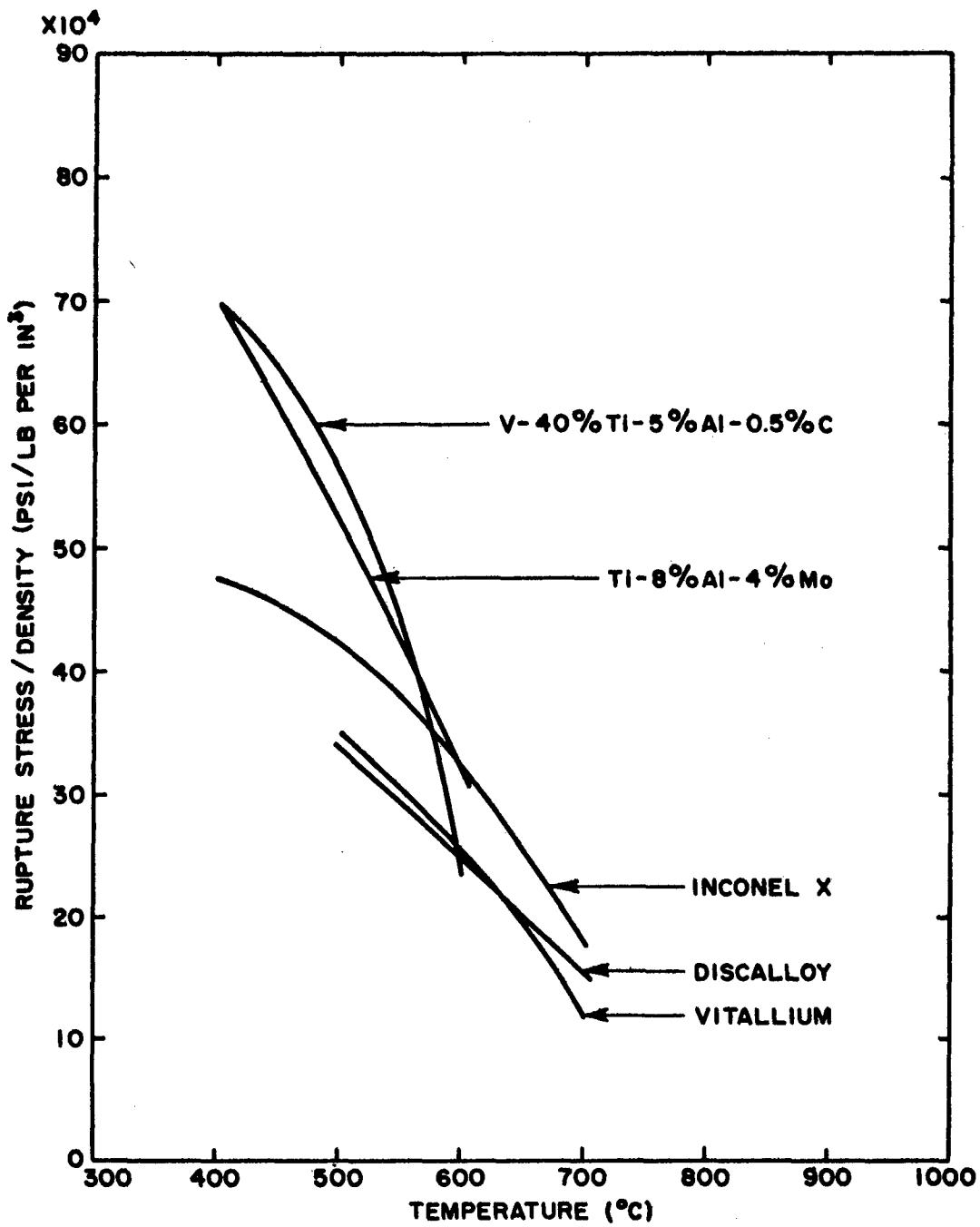
FIG. 26-COMPARATIVE RUPTURE STRESS/DENSITY VERSUS
TEMPERATURE BEHAVIOR OF VARIOUS ALLOYS.

TABLE XX

COMPARISON OF STRESS-RUPTURE PERFORMANCE OF OTHER IMPORTANT ALLOYS

AGAINST THE V-40% Ti-5% Al-0.5% C ALLOY

Alloy	Density $_2$ (Lbs./in.^{2})	(psi) Stress for Rupture in 100 hours	Stress/Density $_3$ (psi/lb. per in.^{3})
24% Ni, 13% Cr. 3% Mo 2.5% Ti, 0.4% Al, 0.8% Mn 0.6% Si, Balance Fe (Discalloy)$_a$	0.28	95,000 (500°C) 70,000 (600°C) 43,000 (700°C)	33.9×10^4 25×10^4 15.4×10^4
73% Ni, 15% Cr, 7% Fe small additions of Cb, Ti, Al (Inconel X)$_{a,b}$	0.307	145,000 (400°C) 130,000 (500°C) 100,000 (600°C) 53,000 (700°C)	47.2×10^4 42.3×10^4 32.5×10^4 17.2×10^4
0.4% C, 26% Cr, 1.5% Ni, 6% W 2% Fe, Balance Co (Vitallium 61)$_b$	0.307	105,000 (500°C) 78,000 (600°C) 35,000 (700°C)	34.2×10^4 25.4×10^4 11.4×10^4
8% Al, 4% Mo, Balance Ti$_c$	0.158	110,000 (400°C) 83,000 (500°C) 50,000 (600°C)	69.9×10^4 52.5×10^4 31.6×10^4
40% Ti, 5% Al, 0.5% C Balance V	0.194	135,000 (400°C) 110,000 (500°C) 46,000 (600°C)	69.6×10^4 56.7×10^4 23.6×10^4

a "Symposium on Strength and Ductility of Metals at Elevated Temperatures". ASTM- Special Technical Publication No. 128, (1952).

b "Metals at High Temperatures", F. H. Clark (Reinhold), 1950.

c Armour Research Foundation Reports.
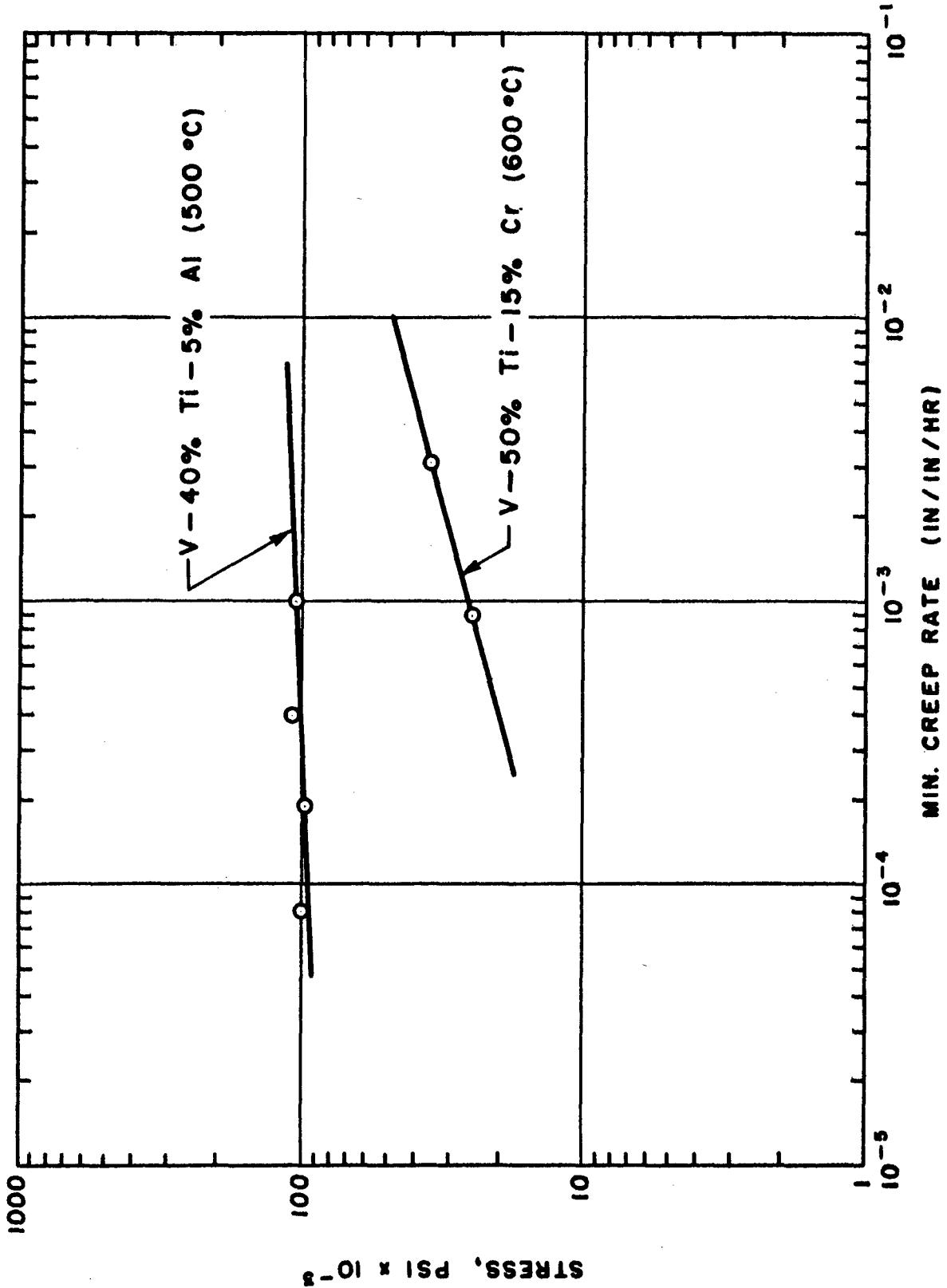
FIG. 27 — CREEP BEHAVIOR OF TWO VANADIUM ALLOYS.

Singular elements in small additions developed anomalous minima in hardnesses and tensile strengths which in some instances were significantly lower than even the unalloyed vanadium itself. Titanium and zirconium were particularly remarkable in this respect. An alloy containing 2.5% zirconium has considerably more tensile ductility than unalloyed vanadium and sheet specimens cold rolled more than 90% reduction in area can still be bent over a sharp mandrel to nearly 180°C.

Nearly all of the forgeable binary alloys proved to have low tensile strengths and negligible tensile ductilities. Outstanding exceptions to this were binary alloys containing up to 50% titanium and up to 3% zirconium. These results showed that the goal of high strength-high ductility could only be achieved in polycomponent alloys based on vanadium-titanium and vanadium-zirconium. On the basis of considerable testing it was shown that only the V-Ti-X alloys (X refers to undesignated third elements) could develop very high strength levels. Single phase solid solution alloys based on vanadium + 40-50% Ti can develop room temperature tensile strengths of up to 170,000 psi.

While the overall strength level of unalloyed vanadium is relatively low, the rate of decrease with temperature is also low with the result that even at 900°C, vanadium retains strengths of the order of 15,000 psi. Judged on a strength to density basis this is nearly equal to molybdenum. A systematic program of hot tensile testing of vanadium alloys showed that the elevated temperature strengths in the range room temperature to 500°C could be raised to a substantially higher level than that obtained for unalloyed vanadium. For instance, unalloyed vanadium at 500°C has a tensile strength of 57,000 psi whereas an alloy containing 50% titanium and 5% silicon had a strength of 158,000 psi. Above 500°C, the alloys showed a sharp progressive drop in strengths with increasing temperature, converging near 900°C. At this temperature, strengths vary between 15,000 psi to 50,000 psi. It would appear that at about 1100°C, all alloys would have about the same strength irrespective of composition.

The excellent high temperature tensile strengths were taken as a preliminary indication of useful creep strengths especially when judged on a strength-to-density basis. The stress-rupture behavior of a number of alloys was studied in the temperature range 500°-700°C. Alloy groups included were V-Ti-Cr, V-Ti-Al, V-Ti-Al-C as well as alloys of V-Ti-Al using alumino-thermic vanadium as an alloy base. The number of alloys tested and the range of composition parameters varied was limited by time and funds. Nevertheless, this limited survey was able to demonstrate that certain vanadium alloys were at least equal to the best that has so far been developed in titanium-base alloys. In the temperature range 400°-550°C there is an unquestioned superiority of the vanadium and titanium alloys over the nickel-base, cobalt-base and iron-base alloys when judged in terms of a stress-to-rupture by density parameter.

Carbon additions have been shown to improve the forging characteristics of vanadium alloys without impairing mechanical properties. In fact, in certain instances, the carbon additions developed superior ductilities. The presence of free carbides does not seem to affect the stress-rupture behavior.

The majority of this work made use of a vanadium metal produced by a calcium reduction process. This metal is of comparatively high purity and is ductile in the unalloyed state. A new vanadium metal is currently available which is produced by an alumino-thermic reduction process. This metal contains appreciable amounts of aluminum in solid solution as well as a higher level of interstitials. Accordingly, it is not ductile in its unalloyed state. It was, however, shown that when used as additions to prepare V + 40-50% Ti + 5-10% Al alloys the alloys were similar in mechanical behavior to the same compositions produced with calcium-reduced vanadium. These superior vanadium alloys by virtue of the current price of alumino-thermic vanadium are competitive with titanium alloys on both a price and property basis. Furthermore, these alloys are not subject to transformation instability as their phase equilibria do not contain mixed phase fields. An exception to this statement is the case of carbon additions. However, there are no indications that aging effects are associated with the presence of carbides.

A considerable proportion of the effort in this program has been devoted to exploring the possibilities of improving the oxidation resistance of vanadium and its alloys. Above the melting point of $V_2O_5(675°C)$, the rate of oxidation is catastrophic. A comprehensive study of 13 binary alloy systems in most cases from 0-100% of the alloying element showed that in no instance could 10% of any alloying element significantly raise the melting point of V_2O_5. Extension of testing to ternary alloys based on vanadium-titanium provided no cases of complete suppression of melting even at 700°C. It was noted that with certain of these alloys, the oxide was rendered considerably more viscous and did not readily drip from the specimen. Systematic measurements of rate of penetration of oxide showed that very considerable deceleration of oxidation rates could be effected by alloying V + 40-50% Ti with chromium and aluminum. It must be stated at this point that the apparent trends of oxidation inhibition were used to guide the selection of alloys for stress-rupture study. In the final analysis it was felt that the best that could be produced in oxidation resistance was insufficient for practical applications. Accordingly, efforts were turned to surface protection methods. It was shown that a nickel electroplating process could provide an oxidation resistant surface capable of operating at as high as 800°C.

In brief recapitulation, it can be stated that vanadium alloys can be produced which are capable of providing interesting and potentially competitive mechanical properties at room temperatures and at elevated temperatures up to 550°C. Furthermore, the mechanical property behavior above 700°C can be evaluated if surface protective measures are taken.

VIII. RECOMMENDATIONS FOR FUTURE WORK

From the present perspective, the most obvious applications for vanadium alloys are in components for use at elevated temperatures where

strength to density conditions are critical. The present scope of effort was confined to the evaluation of the mechanical properties of alloys which had also possibly superior oxidation resistance. In the light of present knowledge that improved oxidation resistance by alloying is not feasible, the scope of alloy additions is widened considerably. It may be pointed out that the highest tensile strengths both at room and elevated temperatures in the V-Ti series occurred in the composition range 10-40% Ti; whereas, the present work was confined to ternary alloys with 40-50% Ti. Since even with this very limited scope it was possible to equal the best of the titanium alloys, it seems very reasonable to expect that a concentration of effort on the creep performance of alloys V-Ti-X with 10-40% Ti will produce alloys of distinctly superior behavior. The possibility of good creep behavior above 600°C should not be ruled out now that use can be made of nickel-plate protection.

APPENDIX

ELECTROPLATING BATHS FOR VANADIUM ALLOYS

For manganese plating the following baths were tried:

1) Chloride bath from unpublished experiments of the Bureau of Standards,

$MnCl_2 \cdot 4H_2O$	325 g/l
NH_4Cl	200 g/l
$(NH_4)_2SO_4$	100 g/l
KSCN	2 g/l

pH = 6-6.5 (maintained with NH_4OH)
CD = 5-10 amps/ft^2
Anode = electrolytic Mn
Bath temperature = room temperature

2) Sulphate bath,

$MnSO_4 \cdot 4H_2O$	100 g/l
$(NH_4)_2SO_4$	75 g/l
NH_4SCN	60 g/l

pH = 4-4.5
CD = 230 amps/ft^2
Anode = electrolytic Mn
Bath temperature = room temperature

3) Chloride bath

$MnCl_2$	175 g/l
NH_4Cl	15 g/l

pH = 2 (maintained with HCl)
CD = 150 amps/ft^2
Anode = electrolytic Mn

The first two baths tried were found unsuitable for plating the selected vanadium alloy (V-40% Ti-5% Al), while the third one seemed successful. One of the problems encountered in all these bath was an increase in the pH factor. The samples, 3/8 in. round and 2 in. long were plated in the following procedure:

1) Electroclean in hot "Orthosil" for about 30 second
2) Rinse
3) Insert in a stirrer and make the specimen anodic for approximately 15 seconds at a current density of about 1 amp/in^2 in the Mn plating bath

4) Reverse the current and plate at the same current density for
30 minutes to get 5 mil thick plate.

Nickel plating

A standard "bright nickel" (trade name, Udylite) bath was used.
The samples were electrocleaned in hot "Orthosil" for about 30 seconds,
rinsed, made anodic in the nickel chloride bath at a current density of
150 amps/ft^2 for 30 seconds. The current was then reversed to cathodic to
be plated at a current density of 80 amps/ft^2 at a rate of 4 mils per hour.
The temperature of the bath was held at 60°C and the samples were rotated
at about 300 rpm. The anode was an electrolytic nickel strip. The
filtration of the bath solution was required to get a very smooth and
adherent plate.